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Planning Document
60721

Volume 1 of 1
Addendum

Work Plan, Field Sampling Plan, and Quality Assurance Project Plan Blackwell Landfill NPL Site

Prepared for:
Forest Preserve District
DuPage County, Illinois

Prepared by:
Warzyn Inc.
Chicago, Illinois

February 1991

WARZYN

February 28, 1991

Mr.Robert Lance, RPM
Mail Code 5HS-11
U.S. EPA Region V
230 South Dearborn St.
Chicago, Illinois 60604

RE: Addendum
Planning Documents
Blackwell Landfill NPL Site

Dear Mr. Lance:

As you have requested, we are sending you 12 copies of the draft Addendum to the Work Plan, Field Sampling Plan, and QAPP Planning Documents for the Blackwell Landfill NPL Site. As suggested in the memorandum dated February 6, 1991 which gave partial approval to the Planning Documents, the water supply wells will be tested for full low-level TCL Organics and low-level TAL Inorganics, rather than for only low-level TCL Volatiles. This Addendum covers the sampling and analysis of water supply wells to include low-level TCL Organics and low-level TAL Inorganics.

Please feel free to contact me if you have any further questions.

Sincerely,

WARZYN INC.

Peter J. Vagt /CAW

Peter J. Vagt
Project Manager

cc. R. Utt, FPD
R. Lanham, IEPA

CAW/kml/TFL
[wpmisc-102-34]
60721

THE PERFECT BALANCE
BETWEEN TECHNOLOGY
AND CREATIVITY

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Volume 1 of 1

Addendum
Work Plan, Field Sampling Plan, and Quality Assurance Project Plan
Blackwell Landfill NPL Site

February 1991

Addendum
February 28, 1991

Work Plan, Field Sampling Plan, and Quality Assurance Project Plan
Blackwell Landfill NPL Site
Remedial Investigation/Feasibility Study
Dupage County, Illinois

Prepared By:

Warzyn Inc.
2100 Corporate Drive
Addison, Illinois 60101
(708) 691-5000

Approvals: Date:

PRP Steering Committee Representative

Warzyn Site Project Director

Warzyn Site Project Manager

Warzyn Site Quality Assurance Officer

U.S. EPA Region V, Remedial Project Manager

U.S. EPA Region V, Quality Assurance Officer

Addendum
Work Plan, Field Sampling Plan, and
Quality Assurance Project Plan
Blackwell Landfill NPL Site RI/FS
DuPage County, Illinois

1.0 PURPOSE

This Addendum to the Blackwell Landfill Site (Site) RI/FS Work Plan, Field Sampling Plan, and Quality Assurance Project Plan (QAPP) discusses modifications and additions to the original project documents. The modifications and additions are the result of the U.S. EPA comments in a memorandum dated February 6, 1991. The memorandum gave partial approval of the Blackwell Landfill QAPP but requested a Work Plan, Field Sampling Plan, and QAPP addendum, which included the sampling and analysis of 26 water supply wells. The 26 water supply wells are located downgradient (25 wells) and in the immediate vicinity (1 well upgradient) of the Blackwell Landfill Site. The water supply wells will be analyzed for target compound list (TCL) organics and target analyte list (TAL) inorganics by low-level detection limit methods.

2.0 ADDENDUM TO THE WORK PLAN

2.1 WATER SUPPLY WELL SAMPLING

2.1.1 Background and Rationale

The Work Plan for the Blackwell Landfill RI/FS includes a water supply well sampling task (Section 4.2.7.2, Task 9), but did not include a complete list of analytical parameters. In addition to TCL volatiles by low-level detection methods, TCL semi-volatiles, pesticides, PCBs, and TAL inorganics will also be analyzed by low-level detection methods for water supply well samples. The exact locations of the water supply wells will be determined after a survey of the private wells in the designated area (see Figures 3-7 and 4-8 of this document) is completed.

The water supply wells identified for sampling, 25 wells downgradient and 1 well upgradient of the Site, will be sampled to assess potential impacts from the Site. The additional parameters were requested to prevent potential data gaps in water supply well information.

3.0 ADDENDUM TO THE FIELD SAMPLING PLAN

3.1 Groundwater Sampling, Water Supply Wells

In addition to low-level analysis of TCL VOCs, water supply wells will also be analyzed for low-level TCL semi-volatiles, pesticides, PCBs, and low-level TAL inorganics. Tables 1, 2, and 3 of the Field Sampling Plan have been modified to reflect the additional parameters required for water supply well samples. Tables 1, 2, and 3 are found in Appendix A of this document.

4.0 ADDENDUM TO THE QUALITY ASSURANCE PROJECT PLAN

4.1 INTRODUCTION

This Addendum describes revisions to the original Blackwell Landfill RI/FS QAPP, dated January 1991. These revisions result from possible data gaps in the water supply well sampling and analysis task. In the following discussion, reference will be made to the original QAPP, through citation of QAPP Element, Sub-Element, and Sub-Task, as applicable.

4.2 QAPP ELEMENTS

Introduction

There are no modifications to this section.

Table of Contents

There are no modifications to this section.

QAPP Element 1.0 Project Description

Sub-Element 1.1 Site Description and Site History

There are no modifications to this QAPP sub-element.

Sub-Element 1.2 Target Compounds

This QAPP sub-element has been modified to include the analysis of water supply wells for low-level detection limit TCL volatiles, semi-volatiles, pesticides, PCBs, and low-level detection limit TAL metals and cyanide. Parameter lists and associated detection limit requirements for the low-level detection limit protocols are contained in Appendices B and C of this Addendum.

Sub-Element 1.3 Project Objectives

This QAPP sub-element has not been modified.

Sub-Element 1.4 Sample Network and Rationale

This QAPP sub-element has been modified such that Tables 1, 2, and 3 of the QAPP include the additional parameter list for water supply wells samples. These tables are found in Appendix A of this document.

Sub-Element 1.5 Project Schedule

There are no modifications to this QAPP sub-element.

QAPP Element 2.0 Project Organization and Responsibilities

Sub-Elements 2.1 Overall Responsibility and 2.2 Monitoring and Sampling Operations and QC

There are no modifications to these QAPP sub-elements.

Sub-Element 2.3 Laboratory Analyses and QC

This QAPP sub-element has been modified to include analysis of water supply well samples for low-level TCL organics, using protocols found in Appendix B of this document by the following laboratory:

Compuchem
3308 Chapel Hill/Nelson Highway
Research Triangle Park, North Carolina 27709

Analysis of water supply well samples for low-level TAL inorganics, using protocols outlined in Appendix C of this document, by the following laboratory:

Warzyn Inc.
One Science Court
Madison, Wisconsin 53711

Sub-Elements 2.4 Specialized Responsibility for Laboratory Analyses, 2.5 Quality Assurance, and 2.6 Performance and Systems Audits

There are no modifications to these QAPP sub-elements.

QAPP Element 3.0 Quality Assurance Objectives for Measurement Data in Terms of Precision, Accuracy, Completeness, Representativeness, and Comparability

This QAPP element has been modified. Table 1 now includes data generating activities and associated data quality objectives for the water supply wells. Table 4 now includes quality control requirements for low-level detection limit analysis of TCL organics and TAL inorganics.

Sub-Element 3.1 Level of Quality Control Effort

Sub-Task 3.1.1 Field Sampling Program

This QAPP sub-task has not been modified.

Sub-Task 3.1.2 Laboratory Analyses

This QAPP sub-task has been modified to include the following QC information:

Compuchem. Analysis of water supply wells for low-level TCL organics will be performed by Compuchem using CLP protocols. Levels of QC effort for these analyses are described in the procedure specified in Appendix B, which provides for low-level detection limits.

Warzyn. Analysis of water supply wells for low-level TAL inorganics will be performed using CLP protocols. Levels of QC effort for these analyses are described in Appendix C of this document.

Sub-Task 3.1.3 Field Measurements

This QAPP sub-task has not been modified.

Sub-Element 3.2 Accuracy, Precision, and Sensitivity of Analyses

Sub-Task 3.2.1 Laboratory Analyses

This QAPP sub-element has been modified to include accuracy and precision requirements for low-level detection limit analyses of TCL organics and TAL inorganics for water supply wells. These requirements are described in the CLP protocol low-level methods outlined in Appendices B and C, respectively, of this document.

Sub-Tasks 3.2.2 Field Sampling Program and 3.2.3 Field Measurements

These QAPP sub-tasks have not been modified.

Sub-Element 3.3 Completeness, Representativeness, and Comparability

This QAPP sub-element has not been modified.

QAPP Element 4.0 Sampling Procedures

This QAPP element has not been modified.

QAPP Element 5.0 Sample Custody and Documentation

Sub-Elements 5.1 Chain of Custody Procedure for Field Activities, 5.2 Chain of Custody Procedure for Laboratory Analysis, and 5.3 Final Evidence File

These QAPP sub-elements have not been modified.

QAPP Element 6.0 Calibration Procedures and Frequency

Sub-Element 6.1 Field Calibration

This QAPP sub-element has not been modified.

Sub-Element 6.2 Laboratory Calibration

This QAPP sub-element has been modified to include procedures and frequency of calibration for low-level TCL organics and low-level TAL inorganics as outlined in Appendixes B and C, respectively, of this document.

QAPP Element 7.0 Analytical Procedures

Sub-Element 7.1 Laboratory Analytical Procedures

This QAPP sub-element has been modified to include the following laboratory analytical procedures:

Compuchem. Water supply samples analyzed by Compuchem for low level TCL organics will follow the procedure outlined in Appendix B of this document.

Warzyn. Water supply well samples analyzed by Warzyn for low level TAL inorganics will follow the procedure outlined in Appendix C of this document.

Sub-Element 7.2 Field Analytical Procedures

This QAPP sub-element has not been modified.

QAPP Element 8.0 Internal Quality Control Check

Sub-Element 8.1 Field

This QAPP sub-element has not been modified.

Sub-Element 8.2 Laboratory

This QAPP sub-element has been modified to include low-level QC requirements. Low-level TCL organic QC requirements are summarized in the procedure outlined in Appendix B of this document. Low-level TAL inorganic QC requirements are summarized in the procedure outlined in Appendix C of this document.

QAPP Element 9.0 Data Reduction, Validation, and Reporting

Sub-Element 9.1 Laboratory Analyses

This QAPP sub-element has been modified to include the following requirements:

Compuchem - Low-level TCL Organics

Requirements for identification, quantification, data reporting, and required data deliverables for the low level TCL organics will follow those in the CLP Statement of Work SOW 2/88 (or most current). Validation of the data will be performed by Warzyn using Laboratory Data Validation Functional Guidelines for Evaluating Organics Analysis, February 1988 in conjunction with QC criteria and detection limit requirements specified with the procedure found in Appendix B of this document.

Warzyn - Low-level TAL Inorganics

Specific procedures for quantification are documented in the methods found in Appendix C of this document. Data reporting and required data deliverables for low level TAL inorganics will follow those in the CLP Statement of Work SOW 7/88 (or most current). Data validation will be performed by Warzyn using Laboratory Data Validation Functional Guidelines for Evaluating Inorganics Analyses, July 1988 in conjunction with QC criteria and detection limit requirements specified within the procedure found in Appendix C of this document.

Sub-Elements 9.2 Field Analyses and 9.3 Field Sampling

These QAPP sub-elements have not been modified.

QAPP Element 10.0 Performance and System Audits

This QAPP element has not been modified.

QAPP Element 11.0 Preventative Maintenance

This QAPP element has been modified to include the following references. Maintenance procedures for laboratory instrumentation and equipment for TCL organics (including low-level TCL organics) are referenced in the CLP Statement of Work SOW 2/88 (or most current). Preventative maintenance procedures for laboratory instrumentation and equipment for TAL inorganics (including low-level TAL inorganics) are referenced in the CLP Statement of Work SOW 7/88 (or most recent).

QAPP Element 12.0 Specific Routine Procedures Used to Assess Data Precision, Accuracy, and Completeness

This QAPP element has not been modified.

QAPP Element 13.0 Corrective Action

This QAPP element has not been modified.

QAPP Element 14.0 Quality Assurance Reports to Management

This QAPP element has not been modified.

Appendix A

Revised Field Sampling Plan and QAPP Tables and Figures

Table 1 - Summary of Data Generating Activities and Associated Data Quality Objectives

Table 2 - Sample Type and Estimated Sample Numbers

Table 3 - Sample Quantities, Containers, Preservatives, and Packaging

Table 4 - Summary of Quality Control Requirements

Figure 3-7 - Locations of Water Supply Wells in Site Vicinity

Figure 4-8 - Private Well Sampling Locations

TABLE 1
SUMMARY OF DATA GENERATING ACTIVITIES AND ASSOCIATED DATA QUALITY OBJECTIVES
BLACKWELL LANDFILL NPL SITE

ACTIVITY	TASK	DESCRIPTION	INTENDED DATA USAGES	ANALYSIS PARAMETERS	DATA QUALITY OBJECTIVE (ANALYTICAL LEVEL)	ANTICIPATED NO. OF INVESTIGATIVE SAMPLES
DEFINE NATURE AND EXTENT OF CONTAMINATION						
Confining Layer Mapping	1	Conduct shallow seismic investigation; make auger probes to bedrock southwest of landfill.	Determine the depth to the bedrock surface and delineate the existence of the clay confining layer in the area west of the landfill.		Level I Data	0
Soil Sampling	2	Conduct soil sampling in areas of past leachate seeps.	To characterize any soil contamination resulting from past leachate seeps.	Analysis of soil samples for TCL and TAL parameters.	Level IV Data for TCL, TAL	3
Surface Water Hydrology	3	Water Level Measurements and Piezometer Installation	To better define the interactions between surface water and groundwater.		Level I Data	0
Surface Water/ Sediment Sampling	4	Surface water and sediment samples taken at locations on Silver, Swim and Supply Lakes and Springbrook.	To document surface water quality surrounding the site and to evaluate the potential contamination effects of discharging groundwater on bottom sediments in surface water bodies surrounding the site.	Analysis of surface water samples for TCL, TAL, indicators and field pH and conductivity. Analysis of sediments for TCL and TAL parameters.	Level IV Data for TCL, TAL Level III Data for Indicators Level I Data for pH and conductivity.	8 Surface Water 8 Sediments
Monitoring Well Construction	5	Installation of 2 additional monitoring well nests (total of 4 monitoring wells).	To better define the "window" where the clay layer may be missing and allowing migration between the upper and lower aquifers.			0
Groundwater Sampling	6	Sampling of 21 existing and the 4 new monitoring wells. Measurement of water levels four times during the investigation.	To evaluate potential groundwater flow paths, assess the groundwater contamination migration pathway, and to characterize the groundwater quality.	Analysis of groundwater samples for TCL, TAL, indicators and field pH and conductivity.	Level IV Data for TCL, TAL Level III Data for Indicators Level I Data for pH and conductivity.	25 Groundwaters
Aquifer Tests	7	Collection of 2 soil samples at each new monitoring well nest location. Samples will represent the upper aquifer and material directly overlying the bedrock.	The upper aquifer samples will be used to assess the upper aquifer material. The material directly over the bedrock will be used to assess the retardative nature of the material and assess its potential to act as an aquitard.	Analysis of soil samples for grain size distribution.	Level III Data	4 Soil Borings

TABLE 1
(CONTINUED)

ACTIVITY	TASK	DESCRIPTION	INTENDED DATA USAGES	ANALYSIS PARAMETERS	DATA QUALITY OBJECTIVE (ANALYTICAL LEVEL)	ANTICIPATED NO. OF INVESTIGATIVE SAMPLES
DEFINE NATURE AND EXTENT OF CONTAMINATION (CONTINUED)						
Meteorological Data Collection	8	Collection of daily temperature, precipitation, wind direction and wind velocity data.	Precipitation records will represent the original source of groundwater, surface water and leachate. Wind directions and velocity data will be used construct wind rose diagrams and will represent probable air migration routes from the site.			0
Additional Water Level Measurements	9	Water levels collected at lower aquifer monitoring wells.	To verify the hydraulic gradient of the lower aquifer.			0
Water Supply Sampling	9	Sampling of 26 water supply wells.	To characterize the water quality and determine if water supply wells have been affected by the contaminant plume.	Analysis of water supply wells for low-level detection TCL organics and TAL inorganics.	Level V Data	26 Water Supply Well Groundwaters
IDENTIFY AND QUANTIFY SOURCES OF CONTAMINATION						
Leachate Volume Evaluation	10	Leachate level measurements at all headwells six times during the investigation.	To estimate leachate volume and generation rate.			0
Landfill Leachate Sampling	11	Sampling of 4 leachate headwells.	To identify the characteristics of the leachate within the landfill.	Analysis of leachate samples for TAL, TCL, COD and indicator parameters.	Level IV Data for TAL, TCL Level III Data for COD and Indicators	4 Leachates
Landfill Gas Sampling	12	Sampling of 2 high flow vents. Measurement of gas flow volume from 24 headwell/vents.	To provide an indication of gas production in various areas of the site. To characterize the landfill gas and to provide for modeling of probable air migration.	Analysis of leachate gas samples for VOCs.	Level V Data	2 Landfill Gas Samples

TABLE 2
SAMPLE TYPE AND ESTIMATED SAMPLE NUMBERS
BLACKWELL LANDFILL NPL SITE

SAMPLE (1) MATRIX	LAB (2)	NO. OF SAMPLES	FIELD DUPLICATES	FIELD (3) BLANKS	MS/MSD (4)	TOTAL NO. SAMPLES	TEST (5,7) PARAMETERS
DEFINE NATURE AND EXTENT OF CONTAMINATION							
Soil Sampling	Warzyn	3	1	0	-	4	TAL Inorganics
	Compuchem	3	1	0	-	4	TCL Volatiles
	Compuchem	3	1	0	-	4	TCL Semivolatiles
	Compuchem	3	1	0	-	4	TCL Pest/PCBs
Surface Water Sampling	Warzyn	8	1	1	-	10	TAL-Inorganics
	Compuchem	8	1	1	1	10	TCL-Volatiles
	Compuchem	8	1	1	1	10	TCL-Semivolatiles
	Compuchem	8	1	1	1	10	TCL-Pest/PCBs
	Warzyn	8	1	1	-	10	Alk,Cl,SO4,TKN, NH3,NO3+NO2,TDS
Sediment Sampling	Warzyn	8	1	0	-	9	TAL-Inorganics
	Compuchem	8	1	0	-	9	TCL-Volatiles
	Compuchem	8	1	0	-	9	TCL-Semivolatiles
	Compuchem	8	1	0	-	9	TCL-Pest/PCBs
Groundwater Monitoring	Warzyn	25	3	3	-	31	TAL-Inorganics
	Compuchem	25	3	3	2	31	TCL-Volatiles
	Compuchem	25	3	3	2	31	TCL-Semivolatiles
	Compuchem	25	3	3	2	31	TCL-Pest/PCBs
	Warzyn	25	3	3	-	31	Alk,Cl,SO4,TKN, NH3,NO3+NO2,TDS
Soil Borings	EWI Eng.	4	1	0	-	5	Grain Size
Water Supply Sampling	Compuchem	26	3	3	2	32	TCL-Volatiles(6)
	Compuchem	26	3	3	2	32	TCL-Semivolatiles(6)
	Compuchem	26	3	3	2	32	TCL-Pest/PCBs(6)
	Warzyn	26	3	3	-	32	TAL-Inorganics(6)

TABLE 2
(Continued)

IDENTIFY AND QUANTIFY SOURCES OF CONTAMINATION

Leachate Headwell Sampling	Warzyn	4	1	1	-	6	TAL-Inorganics
	Compuchem	4	1	1	1	6	TCL-Volatiles
	Compuchem	4	1	1	1	6	TCL-Semivolatiles
	Compuchem	4	1	1	1	6	TCL-Pest/PCBs
	Warzyn	4	1	1	-	6	Alk,Cl,SO4,TKN, NH3,NO3+NO2,TDS, COD
Landfill Gas Vent Sampling	Enseco	2	1	1		4	Volatile Organics

Notes

(1) Samples will be considered low or medium concentration.

(2) Compuchem
3308 Chapel Hill/Nelson Hwy
Research Triangle Park, NC 27709

Warzyn Engineering Inc.
One Science Court
Madison, WI 53705

EWI Engineering
505 Science Court
Madison, WI 53705

Enseco, Inc.
9537 Telstar Ave.
Suite 118
El Monte, CA 91731

(3) A trip blank for VOC analysis will be included with each cooler shipped for aqueous (leachate, groundwater, surface water and water supply wells) samples. One trip blank (pre-cleaned SUMMA passivated canister) is required for the sampling of landfill gas vents for volatiles.

(4) EXTRA VOLUME REQUIREMENT: Extra volume is required for the TCL organic MS/MSD quality control requirement (triple volume for VOC, double volume for BNA and Pesticides/PCBs). TAL inorganics and general water quality indicator parameters require MS/MSD analysis, however, do not require additional sample volume to meet the specified QC.

(5) See Appendix A for EPA TCL and TAL analyte lists.

(6) Low level detection limits required for water supply wells (see Appendices B and C of the QAPP addendum).

(7) Groundwater samples for metals analysis will be field filtered through a 0.45 micron filter prior to the addition of preservatives.

TABLE 3

SAMPLE QUANTITIES, CONTAINERS, PRESERVATIVES, AND PACKAGING
FOR SAMPLES FROM THE BLACKWELL LANDFILL NPL SITE RI/FS

Analysis	Bottles and Jars	Preservation	Holding Time(2)	Volume of Samples	Shipping	Normal Packaging (1)
Low Concentration (Organics)						
Groundwater Samples						
Extractable, Base/neutral, and acids	Two 1-Liter amber glass bottles	Iced to 4°C.	5 days from VTSR to extraction, analysis within 40 days after extraction	Fill bottle to neck	Shipped daily by overnight carrier	Vermiculite
Pesticides/PCBs	Two 1-Liter amber glass bottles	Iced to 4°C.	5 days from VTSR to extraction, analysis within 40 days after extraction	Fill bottle to neck	Shipped daily by overnight carrier	Vermiculite
Volatiles	Two 40-mL volatile organic analysis (VOA) vials.	1:1 HCL (2 drops/ vial), iced to 4°C.	10 days from VTSR	Fill completely no headspace	Shipped daily by overnight carrier	Vermiculite
Water Supply Well Samples						
Extractable, Base/neutral, and acids	Two 1-Liter amber glass bottles	Iced to 4°C.	5 days from VTSR to extraction, analysis within 40 days after extraction	Fill bottle to neck	Shipped daily by overnight carrier	Vermiculite
Pesticides/PCBs	Two 1-Liter amber glass bottles	Iced to 4°C.	5 days from VTSR to extraction, analysis within 40 days after extraction	Fill bottle to neck	Shipped daily by overnight carrier	Vermiculite
Volatiles	Four 40-mL VOA vials	Iced to 4°C.	7 days	Fill completely no headspace	Shipped daily by overnight carrier	Vermiculite

TABLE 3
(Continued)

Analysis	Bottles and Jars	Preservation	Holding Time(2)	Volume of Samples	Shipping	Normal Packaging (1)
Surface Water Samples						
Extractable, Base/neutral, and acids	Two 1-Liter amber glass bottles	Iced to 4°C.	5 days from VTSR to extraction, analysis within 40 days after extraction	Fill bottle to neck	Shipped daily by overnight carrier	Vermiculite
Pesticides/PCBs	Two 1-Liter amber glass bottles	Iced to 4°C.	5 days from VTSR to extraction, analysis within 40 days after extraction	Fill bottle to neck	Shipped daily by overnight carrier	Vermiculite
Volatiles	Two 40-mL VOA vials	1:1 HCL (2 drops/ vial), iced to 4°C.	10 days from VTSR	Fill completely no headspace	Shipped daily by overnight carrier	Vermiculite
Leachate Samples						
Extractable, Base/neutral, and acids	Two 1-Liter amber glass bottles	Iced to 4°C.	5 days from VTSR to extraction, analysis within 40 days after extraction	Fill bottle to neck	Shipped daily by overnight carrier	Vermiculite
Pesticides/PCBs	Two 1-Liter amber glass bottles	Iced to 4°C.	5 days from VTSR to extraction, analysis within 40 days after extraction	Fill bottle to neck	Shipped daily by overnight carrier	Vermiculite
Volatiles	Two 40-mL VOA vials	Iced to 4°C.	7 days	Fill completely no headspace	Shipped daily by overnight carrier	Vermiculite
Low Concentration (Inorganics)						
Groundwater Samples						
Metals	One 1-liter high density polyethylene bottle	Field filter through 0.45 um filter. HNO_3 to pH<2. Iced to 4°C.	180 days from VTSR (26 days from VTSR for mercury)	Fill to shoulder of bottle	Shipped daily by overnight carrier	Vermiculite
Cyanide	One 1-liter high density polyethylene bottle	Add NaOH to pH>12. Iced to 4°C.	12 days from VTSR	Fill to shoulder of bottle	Shipped daily by overnight carrier	Vermiculite

TABLE 3
(Continued)

Analysis	Bottles and Jars	Preservation	Holding Time(2)	Volume of Samples	Shipping	Normal Packaging (1)
Water Supply Well Samples						
Metals	**One 1-liter high density polyethylene bottle**	**HNO_3 to pH<2. Iced to 4°C.**	**180 days from VTSR (26 days from VTSR for mercury)**	**Fill to shoulder of bottle**	**Shipped daily by overnight carrier**	**Vermiculite**
Cyanide	**One 1-liter high density polyethylene bottle**	**Add NaOH to pH>12. Iced to 4°C.**	**12 days from VTSR**	**Fill to shoulder of bottle**	**Shipped daily by overnight carrier**	**Vermiculite**
Surface Water Samples						
Metals	One 1-liter high density polyethylene bottle	HNO_3 to pH<2. Iced to 4°C.	180 days from VTSR (26 days from VTSR for mercury)	Fill to shoulder of bottle	Shipped daily by overnight carrier	Vermiculite
Cyanide	One 1-liter high density polyethylene bottle	Add NaOH to pH>12. Iced to 4°C.	12 days from VTSR	Fill to shoulder of bottle	Shipped daily by overnight carrier	Vermiculite
Leachate Samples						
Metals	One 1-liter high density polyethylene bottle	HNO_3 to pH<2. Iced to 4°C.	180 days from VTSR (26 days from VTSR for mercury)	Fill to shoulder of bottle	Shipped daily by overnight carrier	Vermiculite
Cyanide	One 1-liter high density polyethylene bottle	Add NaOH to pH>12. Iced to 4°C.	12 days from VTSR	Fill to shoulder of bottle	Shipped daily by overnight carrier	Vermiculite
Water Quality Parameters						
Groundwater Samples						
TKN, Nitrate + Nitrite-N and Ammonia	One 1-liter high density polyethylene bottle	H_2SO_4 to pH<2. Iced to 4°C.	28 days	Fill to shoulder of bottle	Shipped daily by overnight carrier	Vermiculite
Alkalinity, Chloride, Sulfate	One 500-mL polyethylene bottle	Iced to 4°C.	28 days (14 days alkalinity)	Fill to shoulder of bottle	Shipped daily by overnight carrier	Vermiculite
TDS	One 500-mL polyethylene bottle	Field filter through 0.45 um filter. Iced to 4°C.	7 days	Fill to shoulder of bottle	Shipped daily by overnight carrier	Vermiculite

TABLE 3
(Continued)

Analysis	Bottles and Jars	Preservation	Holding Time(2)	Volume of Samples	Shipping	Normal Packaging (1)
Surface Water Samples						
TKN, Nitrate + Nitrite-N and Ammonia	One 1-liter high density polyethylene bottle	H_2SO_4 to pH<2. Iced to 4°C.	28 days	Fill to shoulder of bottle	Shipped daily by overnight carrier	Vermiculite
Alkalinity, Chloride, Sulfate	One 500-mL polyethylene bottle	Iced to 4°C.	28 days (14 days alkalinity)	Fill to shoulder of bottle	Shipped daily by overnight carrier	Vermiculite
TDS	One 500-mL polyethylene bottle	Iced to 4°C.	7 days	Fill to shoulder of bottle	Shipped daily by overnight carrier	Vermiculite
Leachate Samples						
TKN, Nitrate+Nitrite-N, Ammonia and COD	One 1-liter high density polyethylene bottle	H_2SO_4 to pH<2. Iced to 4°C.	28 days	Fill to shoulder of bottle	Shipped daily by overnight carrier	Vermiculite
Alkalinity, Chloride, Sulfate	One 500-mL polyethylene bottle	Iced to 4°C.	28 days (14 days alkalinity)	Fill to shoulder of bottle	Shipped daily by overnight carrier	Vermiculite
TDS	One 500-mL polyethylene bottle	Iced to 4°C.	7 days	Fill to shoulder of bottle	Shipped daily by overnight carrier	Vermiculite
Low or Med Concentration (Organics)						
Soil and Sediment Samples						
Extractable, Base/neutral and acids	One 8-oz wide mouth glass jar	Iced to 4°C.	10 days from VTSR to extraction, analysis within 40 days after extraction.	Fill 3/4 full	Shipped daily by overnight carrier	Vermiculite (Med in cans/ vermiculite)
Pesticides/PCBs	One 8-oz wide mouth glass jar	Iced to 4°C.	10 days from VTSR extraction, analysis within 40 days after extraction.	Fill 3/4 full	Shipped daily by overnight carrier	Vermiculite (Med in cans/ vermiculite)
Volatiles	Two 4-oz wide mouth glass jars	Iced to 4°C.	10 days from VTSR	Fill Completely no headspace	Shipped daily by overnight carrier	Vermiculite (Med in cans/ vermiculite)

TABLE 3
(Continued)

Analysis	Bottles and Jars	Preservation	Holding Time(2)	Volume of Samples	Shipping	Normal Packaging (1)
Low or Med Concentration (Inorganics)						
Soil and Sediment Samples						
Metals and Cyanide	One 8-oz wide mouth glass jar	Iced to 4°C.	180 days from VTSR (26 days from VTSR for mercury and 12 days from VTSR for cyanide)	Fill 3/4 full	Shipped daily by overnight carrier	Vermiculite (Med in cans/ vermiculite)
Physical Analysis						
Soil Samples						
Grain Size Distribution	Two 8-oz wide mouth glass jars	NONE	Not established	Fill 3/4 full	Ship by carrier	Vermiculite
Landfill Gas Analysis						
Volatiles	One 6-liter SUMMA passivated canister	Iced to 4°C.	Not established	Fill as described in procedure.	Shipped daily by overnight carrier	Vermiculite

Notes

(1) The packing material should completely cushion the sample bottles - botttom, sides and top.
(2) VTSR - verified time of sampling receipt. Unless otherwise noted, the holding time is from the date sampled.

7210APP01TABLE3
2/22/91addendum
[ccf-400-76b]

TABLE 4
SUMMARY OF QUALITY CONTROL REQUIREMENTS
FOR ANALYSES PERFORMED AT THE BLACKWELL LANDFILL NPL SITE RI/FS

PARAMETER	AUDIT	FREQUENCY[1]	LIMITS[2]
TCL Organics	Requirements per SOW 2/88 (or most current)		
TAL Inorganics	Requirements per SOW 7/88 (or most current)		

TCL Organics (Low Level Detection Limits for Water Supply Wells)

For Volatile Organics:

The acceptance control limits specified in Sections 8, 9, and 11 of the SOP (Appendix B of the QAPP Addendum) should be met. Method blank samples shall be analyzed daily at the beginning of the day before analysis of any samples, and at the beginning of each 12 hour shift. MS/MSD should be analyzed at a frequency of one per group of 20 or fewer samples analyzed.

For Semivolatile Organics:

The acceptance control limits specified in Section 7 and 9 of the SOP (Appendix B of the QAPP Addendum) should be met. Method blank and MS/MSD samples should be prepared and analyzed at a frequency of one per group of 20 or fewer samples analyzed.

For Pesticides/PCBs:

The acceptance control limits specified in Section 7, 8, 9, and 10 of the SOP (Appendix B of the QAPP Addendum) should be met. Method blank and MS/MSD samples should be prepared and analyzed at a frequency of one per group of 20 or fewer samples analyzed.

TAL Inorganics (Low Level Detection Limits for Water Supply Wells)

The QA/QC requirements should be consistent with that of the SOP (Appendix C of the QAPP Addendum).

TABLE 4
(continued)

PARAMETER	AUDIT	FREQUENCY[1]	LIMITS[2]
Alkalinity, Choride, Sulfate, Nitrate+Nitrate Nitrogen			
	Lab Blank	1 per 10 samples	< Detection Limit (DL)
	Check Standard	1 per 10 samples	90 - 110 % Recovery
	EPA QC Reference Standard	1 per set	80 - 120 % Recovery
	Lab Duplicate	1 per 10 samples	10 RPD (± 2xDL if sample concentration is <5 x DL)
	Matrix Spike	1 per 10 samples	85 - 115 % Recovery
	Standard at 2 times detection limit	1 per set after calibration and EPA QC reference standard.	± Instrument DL
Chemical Oxygen Demand			
	Lab Blank	1 per 10 samples	< Detection Limit (DL)
	Check Standard	1 per 10 samples	90 - 110 % Recovery
	EPA QC Reference Standard	1 per set	80 - 120 % Recovery
	Lab Duplicate	1 per 10 samples	10 RPD (± 2xDL if sample concentration is <5 x DL)
	Matrix Spike	1 per 10 samples	85 - 115 % Recovery
Ammonia Nitrogen			
	Lab Blank	1 per 10 samples	< DL
	Preparation Blank	1 per set	< DL
	Check Standard	1 per 10 samples	90 - 110 % Recovery
	EPA QC Reference Standard	1 per set	80 - 120 % Recovery
	Lab Duplicate	1 per 10 samples	10 RPD (± 2xDL if sample concentration is <5 x DL)
	Matrix Spike	1 per 10 samples	85 - 115 % Recovery

TABLE 4
(continued)

PARAMETER	AUDIT	FREQUENCY[1]	LIMITS[2]
TKN			
	Lab Blank	1 per 10 samples	< DL
	Preparation Blank	1 per set	< DL
	Check Standard	1 per 10 samples	90 - 110 % Recovery
	EPA QC Reference Standard	1 per set	80 - 120 % Recovery
	Lab Duplicate	1 per 10 samples	10 RPD (± 2xDL if sample concentration is <5 x DL)
	Matrix Spike	1 per 10 samples	85 - 115 % Recovery
Total Dissolved Solids			
	Lab Blank	1 per set	< DL
	EPA QC Reference Standard	1 per set	80 - 120 % Recovery
	Lab Duplicate	1 per 10 samples	10 RPD (± 2xDL if sample concentration is <5 x DL)
Grain Size Distribution			
	Lab Duplicate	1 per 10 samples	10 RPD or <2% by weight
Field pH			
	Check Standard	1 per 10 samples	± 0.05 pH unit of buffer selection
	Duplicate	1 per 10 samples	± 0.2 pH unit
Field Specific Conductance			
	Check Standard	1 per 10 samples	± 5% of standard
	Duplicate	1 per 10 samples	15 RPD (± 2xDL if sample concentration is <5 x DL)

TABLE 4
(continued)

PARAMETER	AUDIT	FREQUENCY[1]	LIMITS[2]
Volatile Organic Compounds (for leachate gas samples)			
	Check Standard	One standard containing all target compounds (after initial tuning)	90 % of the target compounds must be within ± 30 % of the 3 point calibration curve.
	Lab Control Sample and Duplicate Control Sample (containing 5 specified compounds)	1 per 20 samples	85 - 115 % and <20 RPD (for all 5 compounds)
	System Blank	1 per 20 samples	All compounds < MDL

1 Frequencies apply to each individual matrix.
2 Refer to Appendix A for required detection limits for each analyte.

721QAPP01TABLE4
2/22/91addendum
[ccf-400-76c]

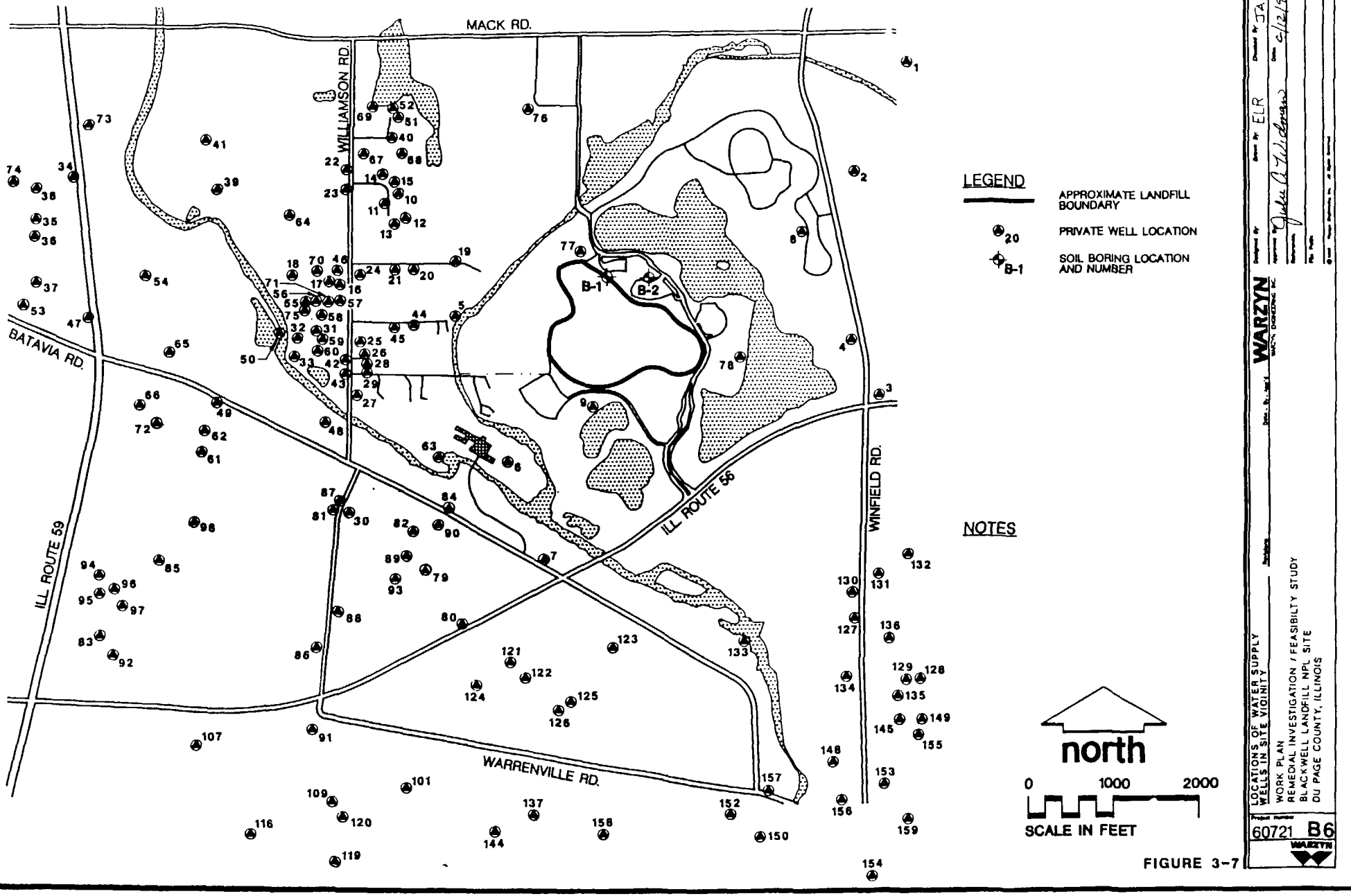
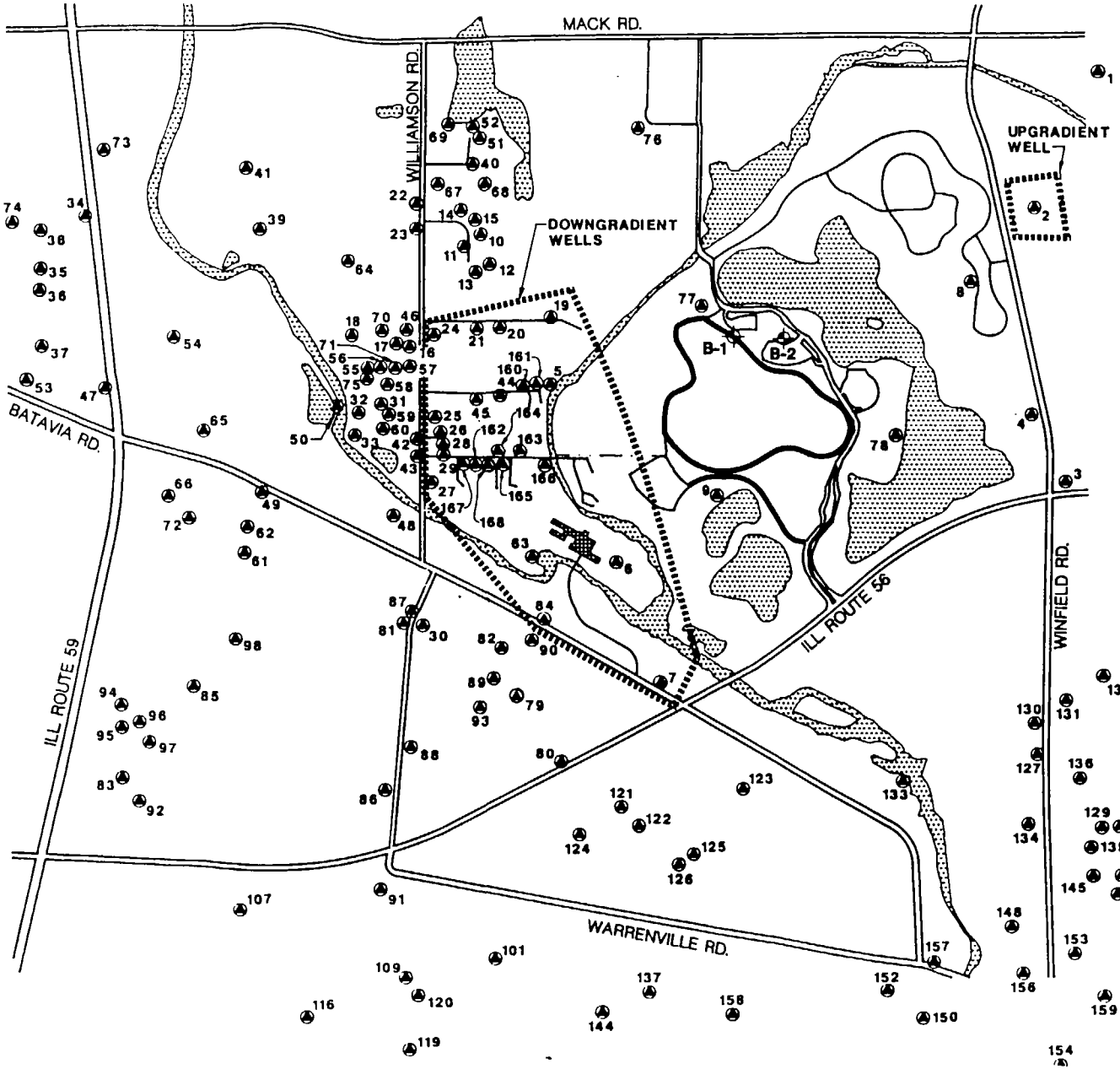

MACK RD.
WILLIAMSON RD.
BATAVIA RD.
ILL ROUTE 59
ILL ROUTE 56
WINFIELD RD.
WARRENVILLE RD.
B-1
B-2
LEGEND
APPROXIMATE LANDFILL BOUNDARY
PRIVATE WELL LOCATION
SOIL BORING LOCATION AND NUMBER
NOTES
north
0 1000 2000
SCALE IN FEET
LOCATIONS OF WATER SUPPLY WELLS IN SITE VICINITY
WORK PLAN
REMEDIAL INVESTIGATION / FEASIBILITY STUDY
BLACKWELL LANDFILL NPL SITE
DU PAGE COUNTY, ILLINOIS
WARZYN
60721 B6

FIGURE 3-7



LEGEND

- APPROXIMATE LANDFILL BOUNDARY
- 20 PRIVATE WELL LOCATION
- B-1 SOIL BORING LOCATION AND NUMBER

NOTES

1. PRIVATE WELLS INSIDE BOXED AREAS WILL BE SAMPLED.

north

0 1000 2000

SCALE IN FEET

FIGURE 4-8

PRIVATE WELL SAMPLING LOCATIONS

WORK PLAN
REMEDIAL INVESTIGATION / FEASIBILITY STUDY
BLACKWELL LANDFILL NPL SITE
DU PAGE COUNTY, ILLINOIS

Designed by ELR Drawn by JAW Date 4/12/90

WARZYN ENGINEERING INC.

60721B22

Appendix B

Compuchem Laboratories
Low-Level Detection Methods for Residential Well Sample Analysis

Volatile Organics
Semi-Volatile Organics
Pesticides/PCBs

Volatile Organics

STANDRAD OPERATING PROCEDURE

FOR

THE ANALYSIS OF VOLATILE ORGANICS WITH LOW DETECTION LIMITS

IN RESIDENTIAL WELL WATER SAMPLES

USING GAS CHROMATOGRAPHY/MASS SPECTROMETRY

PREPARED BY

Cheng-Wen Tsai

October 1987

Revised January 1989

Revised May, 1989

ANALYSIS OF VOLATILE ORGANICS WITH LOW DETECTION LIMITS

BY

PURGE AND TRAP GAS CHROMATOGRAPHY/MASS SPECTROMETRY METHOD

(PREPARED BY CHENG-WEN TSAI)

REVISED JANUARY 1989
Revised May, 1989

1.0 SCOPE AND APPLICATION

1.1 This standard operating procedure describes the method for the analysis of volatile organics in private well, municipal water supply and domestic well samples.

1.2 This is a purge and trap gas chromatography/mass spectrometry (GC/MS) method applicable to the determination of 38 compounds (See Table 1) in municipal water supply, and private well water samples.

1.3 The required method detection limit (MDL) for each compound is listed in Table 1.

1.4 This method is restricted to use by or under the supervision of analysts experienced in the operation of a purge and trap system, and gas chromatography/mass spectrometry, and in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Section 10.

2.0 SUMMARY OF METHOD

2.1 An inert gas is bubbled through a 20-ml water sample contained in a specially designed purging chamber at ambient temperature. The purgeables are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent trap where the purgeables are trapped. After purging is completed, the trap is heated and backflushed with the inert gas to

TABLE 1

TARGET COMPOUND LIST (TCL) AND QUANTITATION LIMITS (QLs)

(FOR RESIDENTIAL WELL WATER SAMPLES)

VOLATILE ORGANICS	CAS NUMBER	QUANTITATION LIMITS(u
Benzene	71-43-2	1.5
Bromdichloromethane	75-27-4	1.5
Bromoform	75-25-2	1.5
Bromomethane	74-83-9	1.5
Carbon Tetrachloride	56-23-5	1.5
Chlorobenzene	108-90-7	1.5
Chloroethane	75-00-3	1.5
Chloroform	67-66-3	1.5
Chloromethane	74-87-3	1.5
Dibromochloromethane	124-48-1	1.5
1,1-Dichloroethane	75-34-3	1.5
1,2-Dichloroethane	107-06-2	1.5
1,1-Dichloroethene	75-35-4	1.5
1,2-Dichloroethene (Total)		1.5
1,2-Dichloropropane	78-87-5	1.5
Cis-1,3-Dichloropropene	10061-01-5	2.0
Trans-1,3-Dichloropropene	10061-02-6	2.0
Ethyl Benzene	100-41-4	1.5
Methylene Chloride (*)	75-09-2	2.0
1,1,2,2-Tetrachloroethane	79-34-5	1.5
Tetrachloroethene	127-18-4	1.5
Toluene (*)	108-88-3	1.5
1,1,1-Trichloroethane	71-55-6	1.5
1,1,2-Trichloroethane	79-00-5	1.5
Trichloroethene	79-01-6	1.5
Vinyl Chloride	75-01-4	1.5
Acrolein	107-02-8	25.0
Acetone (*)	67-64-1	5.0
Acrylonitrile	107-13-1	25.0
Carbon Disulfide	75-15-0	3.0
2-Butanone (*)	78-93-3	5.0
Vinyl Acetate	108-05-4	5.0
4-Methyl-2-Pentanone	108-10-1	1.5
2-Hexanone	519-78-6	5.0
Styrene	100-42-5	1.0
m-Xylene **	108-38-3	1.5

O-Xylene **	95-47-6	1.5
p-Xylene **	106-42-3	1.5

NOTE: * Common laboratory solvent. Control limits for blanks are 5 the method detection limits.

** m-Xylene, o-Xylene and p-Xylene are reported as a total of three.

desorb the purgeables onto a gas chromatographic column. The gas chromatograph is temperature programmed to separate the purgeables which are then detected with mass spectrometer.

3.0 INTERFERENCES

3.1 Impurities in the purge gas, organic compounds outgasing from the plumbing ahead of the trap, and solvent vapors in the laboratory account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running laboratory reagent blanks. The use of non-telfon plastic tubing, non-telfon thread sealants, or flow controllers with rubber components in the purge and trap system should be avoided.

3.2 Samples can be contaminated by diffusion of volatile organics through the septum seal into the sample during shipment and storage. A trip blank sample prepared from organic-free water and carried through the sampling and handling protocol can serve as a check on such contamination.

3.3 Contamination by carry-over can occur whenever high level and low level samples are sequentially analyzed. To reduce carry-over, the purging device and sample syringe must be rinsed with reagent water between sample analysis. Whenever an unusually concentrated sample is encountered it should be followed by an analysis of reagent water to check for cross contamination. It may be necessary to wash the purging device with a detergent solution, rinse it with distilled water, and then dry it in a 105°C oven between analysis. The trap and other parts of the system are also subjected to contamination; therefore, frequent bakeout and purging of the entire system may be required.

4.0 SAFETY PRECAUTIONS

4.1 The toxicity or carcinogenicity of chemicals used in this method has not been precisely defined, each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized. Each laboratory is responsible for maintaining awareness of OSHA regulations regarding safe handling of chemicals

used in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available for the information of the analysts.

4.2 The following parameters covered by this method have been tentatively classified as known or suspected human or mammalian carcinogens: benzene, 1,4-dichlorobenzene, hexachlorobutadiene, tetrachloroethene, trichloroethene, carbon tetrachloride, bis-2-chloroisopropyl ether, 1,2-dichloroethane, 1,1,2,2,-tetra-chloroethane, 1,1,2-trichloroethane, chloroform, 1,2-dibromo-methane, and vinyl chloride. Primary standards of these toxic compounds should be prepared in a hood. NIOSH MESA approved toxic gas respirator should be worn when the analysts handle high concentrations of these toxic compounds.

5.0 APPARATUS AND MATERIALS

5.1 Sample Containers

Forty milliliter (40-ml) screw cap glass vials with PTFE-faced silicone septum seals should be used. Wash vials and seals with detergent, rinse with tap water, then distilled water, and dry at 105^{0}C, allow to cool in area known to be free of organic vapors.

5.2 purge and Trap System (Tekmar LSC-2 or equivalent)

5.2.1 Purging Device

The all glass purging device must be capable of accepting 20-ml samples withn a water column at least 5-cm deep. A glass frit installed at the base of sample chamber allowing purging gas to pass through the water column as finely divided bubbles with a diameter of 3 cm at the origin.

5.2.2 Volatile Trap

The trap must be at least 25 cm long and have an inside diameter of at least 0.105 inches. The trap must contain the following amounts of adsorbents: 1/3 of 2,6-diphenylene oxide polymer, 1/3 of silica gel, and 1/3 of coconut charcoal. Prior to daily use, the trap is conditioned for 10 minutes at 220^{0}C while backflusing with an

inert gas flow of at least 20 ml/min. The trap effluent is vented to the room through a charcoal trap.

5.2.3 Desorber

The desorber must be capable of rapidly preheating the trap to 180°C, then desorbing the trap to the GC column while maintaining the temperature of 180°C.

5.3 GC/MS SYSTEM

5.3.1 Gas Chromatograph (Hewlet Parkard 5993 GC or Equivalent)

Gas chromatograph must be capable of temperature programming and achieving an initial column temperature of 30°C - 45°C. Variable constant differential flow controllers capable of maintaining constant flow rates throughout the desorption and temperature program should be used.

5.3.2 Gas Chromatographic Column

Eight Ft. long x 1/8 O.D. glass column, packaed with 1% SP-1000 on Carbopack B (60/80 mesh) or equivalent.

5.3.3 Mass Spectrometer (Finnigan 5100 MS or equivalent)

Must be capable of scanning from 20 to 260 amu every 7 seconds or less, utilizing 70 V (nominal) electron energy in the electron impact ionization mode, and producing a mass spectrum which meet all the criteria in Table 3 when 50 ng of 4-bromofluorobenzene (BFB) is injected through the GC inl

5.3.4 GC/MS Interface

GC to ms interface constructed of all glass or glass lined materials should be used. Glass can be deactivated by silanizing with dichlorodimethylsilane.

5.3.5 Data System

A computer system must be interfaced to the mass

spectrometer that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained through the duration of the chromatographic program. The computer must have the software that allows searching any GC/MS data file for spectra m/z (masses) and plotting such m/z abundance versus time or scan number. Software must also allow integrating the abundance in any Extracted Ion Current Profile (EICP) between specific time or scan number limits.

5.3.6 Syringe and Syringe Valves

5.3.6.1 Syringes - 5-ml and 25-ml glass hypodermic with luerlock tip (two each).

5.3.6.2 Micro Syringes - 25- and 100-ul.

5.3.6.3 Gas Syringes - 1.0 and 5.0 ml gas tight, with shut-off valve.

5.3.7 Miscellaneous

5.3.7.1 Standard Storage Containers - 3.7 ml screw cap amber vilas.

5.3.7.2 Mininert Valves - Screw cap.

6.0 REAGENTS

6.1 Methanol, demonstrated to be free of analytes (spike 100 ul into 25 ml of reagent water and analyze. Result should be less than detection limits.).

6.2 Reagent water, producing less than detection limits of those compounds that are monitored. Prepared by boiling distilled or natural waters for 15 minutes followed by 1 hour purge with inert gas while temperature is held at 90^0C or carbon filtered. Store in clean, narrow mouthed crip top PTFE-lined septa bottles.

6.3 Stock Standards - Commerical mixed stock solutions are available (Supelco Purgeeables A, B, and C) that contain most of the compounds of interest at a concentration of 0.2 mg/ml. Stock solutions must be prepared from neat, as folows for those compounds not included

in the commerical mixes(NOTE 1).

6.3.1 Place 24.4 ml of methanol in a 25-ml volumetric flask. Allow flask to stand unstoppered for 10 minutes or until all alcohol-wetted surfaces have dried, and then tare.

6.3.2 Using a 100-ul syringe, add 50 mg of assayed reference material to the flask. Be sure that the drops fall directly into the alcohol without contacting the neck of the flask. Retare the flask and add 50 mg of the next compound. Repeat the process until all compounds have been added.

6.3.3 Dilute to volume, and stopper. Mix by inverting flask several times. The resulting solution will contain each analyte at a concentration of 2.0 mg/ml.

6.3.4 Store stock standard solutions in 3-ml vials equipped with PTFE mininert valve tops at 0^{0}C. All standards must be replaced each month.

NOTE 1: The following compounds must be made from neat: Cis-1,2-dichloroethene, trans-1,2-dichloroethene, O-xylene, m-xylene, p-xylene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, styrene, 1,2-dichlorobenzene.

6.4 Secondary Dilution Standards

Using stock standards to prepare secondary dilution standards in methanol. The secondary dilution standards are prepared at concentrations that can be easily diluted to prepare aqueous calibration standards that will bracket the working range of the method.

6.4.1 To prepare secondary dilution standards, place 9.0 ml of methanol into a 10-ml volumetric flask.

6.4.2 Inject exactly 250 ul of the speclco purgeable A and purgeable B stock solution, and 250 ul of the stock solution prepared from neat (6.3) into the methanol. When the standard solution is

prepared as above; the solution will contain each analyte at a concentration of 5 ng/ul.

6.4.3 Separate secondary dilution standard mixture should be prepared weekly for the gases from the Supelco purgeable C mix.

6.4.4 Store secondary dilution standards in 3-ml glass vials equipped with PTFE mininert valve screw tops. Storage conditions and time described for stock standary solutions (6.3.4) also apply to the secondary dilution standard solutions.

6.5 Working Aqueous Calibration Standards

Using the secondary dilution standards to prepare five calibration standards at concentrations of 5, 10, 20, 40 and 60 ug/L for all volatile compounds except the acrolein and acrylonitrile, which should be at concentrations of 25, 50, 75, 100 and 125 ug/L.

6.6 Continuing Calibration Check Standard

Prepare the aqueous continuing calibration check standard solution at concentration of 20 ug/L for all compounds except acrolein and acrylonitrile, which should be at concentration of 50 ug/L.

6.7 Sample matrix Spiking Solution

Prepare a matrix spiking solution containing all compounds of interest in methanol using the procedures described in Section 6.3 and 6.4. It is recommended that the secondardy dilution standard be prepared at a concentration of 50 ug/mL for all compounds except acrolein and acrylonitrile, which shall be at a concentration of 125 ug/mL. The addition of 10 uL of such standard solution to 25 mL of reagent water or samples would be equivalent to 20 ug/L. Store at 0°C. The sample matrix spiking solution should be discarded after 1 month.

6.8 Internal Standard Solution

Prepare a spiking solution containing Bromochloromethane, 1,4-Difluorobenzene, and chlorobenzene-d5 in methanol using the procedures described in Section 6.3 and 6.4. It is recommended that the secondary dilution standard be prepared at a concentration of 50 ug/mL of each internal standard compound. The addition of 10 uL of such a standard to 25 mL of sample or calibration standard would be equivalent to 20 ug/L.

6.9 Surrogate Spike Standard Solution

Prepare a surrogate spiking solution containing Toluene-d8, Bromofluorobenzene, and 1,2-dichloroethane-d4 in methanol using the procedures described in Section 6.3 and 6.4. It is recommended that the secondary dilution standard be prepared at a concentration of 50 ug/mL of each surrogate spike compound. The addition of 10 uL of such as standard to 25 mL of sample or calibration standard would be equivalent to 20 ug/L.

6.10 4-BORMOFLUOROBENZENE (BFB) Solution

Prepare a 25 ug/mL solution of bromofluorobenzene in methanol. This solution would be used for MS tuning.

7.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

7.1 Sample collection

7.1.1 Collect all samples in duplicate(2 40-ml glass vials). Fill sample bottles to overflowing. No air bubbles should pass through the sample as the bottle is filled, or be trapped in the sample when the bottle is sealed.

7.1.2 When sampling from a water tap, open the tap and allow the system to flush until water temperature has stabilized (usually about 10 minutes). Adjust the flow to about 500 ml/min. and collect duplicate samples from the flowing system.

7.1.3 When sampling from an open body of water, fill a 1-quart wide-mouth bottle or 1-liter beaker with sample from a respresentative area, and

carefully fill duplicate sample bottles from the container.

7.2 Sample Preservation

7.2.1 Adjust the pH of the duplicate samples to <2 by carefully adding one drop of 1:1 HCl for each 20 ml of sample volume (See Reference No.6). Seal the sample bottles, PFTE-face down, and shake vigorously for one minutes.

7.2.2 The samples must be chilled to 4^0C on the day of collection and maintained at that temperature until analysis. Field samples that will not be packaged for shipment with sufficient ice to ensure that they will be at 4^0C on arrival at the laboratory.

7.3 Sample storage

7.3.1 Store samples at 4^0C until analysis. The sample storagearea must be free of organic solvent vapors.

7.3.2 Analyze all samples within 7 days of collection. Samples not analyzed within this period must be discarded and replaced.

8.0 CALIBRATION AND STANDARDIZATION

8.1 Tuning and GC/MS Calibration

8.1.1 The laboratory must establish that a given GC/MS system meet the standard spectral abundance criteria prior to initiating any on-going data collection. The GC/MS system must be hardware tuned to meet the abundance criteria listed in Table 4 for a maximum of a 50 ng injection of 4-Bromofluorobenzene (BFB). Add 50 ng of BFB solution to 20 ml of reagent water and analyze alone. BFB should NOT be analyzed simultaneously with any calibration standards or blanks. This criteria must be demonstrated dialy or for each twelve-hour (12) time period. If required, background substraction must be straight forward and designed only to eliminate column bleed or instrument background.

8.1.2 BFB criteria MUST be met before any standards, samples or blanks are analyzed.

8.1.3 Any action taken which may results in effecting the tuning criteria for BFB, the tune must be verified irrespective of the twelve-hour tuning requirement.

8.1.4 The laboratory shall document the GC/MS tuning and mass calibration each time the system is tune.

8.2 Calibration of GC/MS System

8.2.1 Initial Internal Standard Calibration

8.2.1.1 Prior to the analysis of samples and required blanks and after tuning criteria have been met, the GC/MS system must be initially calibrated at a minimum of five concentrations to determine the linearity of response utilizing the initial calibration standard solutions containing all compounds listed in Table 2. Once the system has been calibrated, the calibration must be verified after the initial calibration and each twelve(12) hours time period for each GC/MS system.

TABLE 2

CHARACTERISTIC IONS FOR VOLATILE ORGANIC COMPOUNDS

Parameters	Primary Ion	Secondary Ions
Chloromethane	50	52
Bromomethane	94	96
Vinyl Chloride	62	64
Chloroethane	64	66
Methylene Chloride	84	49, 51, 86
Acetone	43	58
Carbon Disulfide	76	78
1,1-Dichloroethene	96	61, 98
1,1-Dichloroethane	63	65, 83, 85, 98, 100
1,2-Dichloroethene	96	61, 98
Chloroform	83	85
1,2-Dichloroethane	62	64, 100, 98
2-Butanone	72	57
1,1,1-Trichloroethane	97	99, 117, 119
Carbon Tetrachloride	127	119, 121
Vinyl Acetate	43	86
Bromodichloromethane	83	85
1,1,2,2-Tetrachloroethane	83	85, 131, 133, 166
1,2-Dichloropropane	63	65, 114
Trans-1,3-Dichloropropene	75	77
Trichloroethene	130	95, 97, 132
Dibromochloromethane	129	208, 206
1,1,2-Trichloroethane	97	83, 85, 99, 132, 134
Benzene	78	-
Cis-1,3-Dichloropropene	75	77
Bromoform	173	171, 175, 250, 252, 254,
2-Hexanone	43	58, 57, 100
4-Methyl-2-pentanone	43	58, 100
Tetrachloroethene	164	129, 131, 166
Toluene	92	91
Chlorobenzene	112	114
Ethyl Benzene	106	91
Styrene	104	78, 103
Total Xylenes	106	91

The primary ion should be used unless interferences are present, in which case, a secondary ion may be used.

TABLE 3

VOLATILE INTERNAL STANDARDS WITH CORRESPONDING TCL ANALYTES ASSIGNED FOR QUANTITATION

Bromochloromethane	1,4-Difluorobenzene	Chlorobenzene-d_5
Chloromethane	1,1,1-Trichloroethane	2-Hexanone
Bromomethane	Carbon Tetrachloride	4-Methyl-2-Pentanone
Vinyl Chloride	Vinyl Acetate	Tetrachloroethene
Chloroethane	Bromodichloromethane	1,1,2,2-tetra-chloroethane
Methylene Chloride	1,2-Dichloropropane	Toluene
Acetone	Trans-1,3-dichloropropene	Chlorobenzene
Carbon Disulfide	Trichloroethene	Ethylbenzene
1,1-dichloroethene	Dibromochloromethane	Styrene
1,1-dichloroethane	1,1,2-Trichloroethane	Xylene (total)
1,2-Dichloroethene(Total)	Benzene	Bromofluorobenzene (Surrogate)
Chloroform	Cis-1,3-dichloropropene	
1,2-Dichloroethane	Bromoform	Toluene-d_8(surrogate)
2-Butanone		
1,2-Dichloroethane-d_4 (surrogate)		

TABLE 4

p-BROMOFLUOROBENZENE (BFB) KEY IONS AND ABUNDANCE CRITERIA

Mass	Ion Abundance Criteria
50	15.0 - 40.0 % of the base peak
75	30.0 - 60.0 % of the base peak
95	Base peak, 100 % relative abundance
96	5.0 - 9.0% of the base peak
173	Less than 1.00% of the base peak
174	Greater than 50.0% of the base peak
175	5.0 - 9.0% of mass 174
176	Greater than 95.0%, but less than 101.0% of mass 174.

NOTE: BFB criteria MUST be met before any samples, sample extracts, blanks, or standards are analyzed.

8.2.1.2 Prepare calibration standards by spiking five portions of 20 ml reagent waters with various amount of secondary dilution standard solution (6.4) to yield the following specific concentrations: 5, 10, 20, 40, and 60 ug/L for all compounds except acrolein and acrylonitrile, which have the specific concentrations at 25, 50, 75, 100 and 125 ug/L.

Internal standards and surrogate spike standards will be added to each each calibration standard solutions to yield a concentration of 20 ug/L.

8.2.1.3 Analyze each calibration standard solution and tabulate the area of the primary characteristic ion againt concentration for each compound including all required internal standards and surrogate standard compounds. The relative retention time (RRT) of each compound in each calibration run should agree within 0.06 RRT units.

8.2.1.4 Use Table 4 and Equation 1 to calculate the relative response factor (RRF) for each compound at each concentration level.

$$RRF = \frac{A_x}{A_{is}} \times \frac{C_{is}}{C_x} \qquad \text{Equation}$$

Where,

A_x = Area of the characteristic ion for the compound to be measured.

A_{is} = Area of the characteristic ion for the specific internal standards from Table 2.

C_{is} = Concentration of the internal standard (ng/UL).

C_x = Concentration of the compound to be measured (ng/uL).

8.2.1.5 Use equation 2 and the relative response factors (RRF) from the initial calibration to calculate the relative standard deviation (%RSD) for compounds labelled as calibration check compounds in Table 4.

$$\%RSD = \frac{SD}{X} \times 100 \qquad \text{Equation 2}$$

Where,

RSD = Relative Standard Deviation

SD = Standard Deviation of initial relative response factors (per compound).

$$\text{Where : } SD = \sqrt{\sum_{i=1}^{N} \frac{(X_i - X)^2}{N-1}} \qquad \text{Eq. 3}$$

X = Mean of initial relative response factors (per compound

The %RSD for each individual calibration check compound must be less than or equal to 30.0%. This criteria must be met for the initial calibration to be valid.

8.2.1.6 System Performance Check

A system performance check must be performed to insure that minimum average relative response factors are met before the calibration curve is used. This is done by analyzing five system check compounds (SPCCs): Chloromethane, 1,1-dichloroethane, bromoform, 1,1,2,2-tetrachloroethane, and chlorobenzene. The minimum acceptable RRF for these compounds is 0.300 (0.100 for bromoform, and 0.200 for 1,1,2,2-tetrachloroethane).

8.2.1.7 The initial calibration is valid only after

both the %RSD for calibration check compound and the minimum RRF for SPCC have been met. Only after both of these criteria are met ca sample analysis begin.

8.3 Continuing Calibration Check

8.3.1 A calibration standard(s) containing all volatile organics listed in Table 2, including all required surrogate compounds, must be analyzed each twelve hours during analysis. The concentration of each compound in the continuing calibration check (CCC) is 20 ug/L except acrolein and acrylonitrile (50 ug/L). Compare the relative response factor data from the standards each twelve hours with the average relative response factor from the initial calibration for a specific instrument. A system performance check must be made each twelve hours. If the SPCC criteria are met, a comparison of relative response factors is made for all compounds.

8.3.2 After the system performance check is met, use equation 4 to calculate the percent difference (% difference) for all calibration check compounds in Table 4 in order to check the validity of the initial calibration.

8.3.2.1 Calculate the percent difference using Equation 4.

$$\%\text{Difference} = \frac{RRF_I - RRF_C}{RRF_I} \times 100 \qquad \text{Eq. 4}$$

Where

RRF_I = Average relative response factor from initial calibration.

RRF_C = Relative response factor from current calibration check.

8.3.2.2 If the percent difference for any compound is greater than 20%, the laboratory should consider this a warning limit. If the percent difference for each CCC is less

than or equal to 25.0%, the initial calibration is assumed to be valid. If the criteria are not met (>25.0% difference), for any one of the calibration check compound, corrective action MUST be taken. Problems similar to those listed under SPCC could affect this criteria. If no source of the problem can be determined after corrective action have been taken, a new initial five points calibration MUST be generated. These criteria MUST be met before sample analysis begins.

9.0 QUALITY CONTROL

9.1 Each laboratory that uses this method is required to operate formal quality control program. The minimum requirements of this program consists of an intial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and document data quality. The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established perfromance criteria to determine if the results of analysis meet the performance characteriztics of the method. A quality control check standard must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

9.1.1 The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method. This ability is established as are described in Section 9.2 .

9.1.2 In recognition of advances that are occurring in chromatography, the analyst is permitted certain options (detailed in Section 10.2.2) to improve the separation or lower the cost of measurements. Each time such a modification is made to the method, the analyst is required to repeat the procedure in Section 9.2 .

9.1.3 Each day, the analyst must analyze a reagent water blank to demonstrate that interferences from the analytical system are under control.

9.1.4 The laboratory must, on an ongoing basis, demonstrate through the analyses of quality control check standards that the operation of the measurement system is in control. The frequency of the check standard analyses is equivalent ot 10% of all samples analyzed but at least two samples per month. Using the following procedure to analyze a quality control check sample for all analytes of interest at 10 ug/L:

9.1.4.1 Prepare a QC check sample by adding 50 ul of QC check sample concentrate to 20 ml of reagent water in a glass syringe.

9.1.4.2 Analyze the QC check sample according to Section 10, and calculate the recovery for each analyte. The recovery must be between 60% and 140% of the expected values.

9.1.4.3 If the recovery for any analyte falls outside the designated range,the analyte has failed the acceptance criteria. A check standard containing each analyte that failed must be re-analyzed.

9.1.5 On a weekly basis, the laboratory must demonstra the ability to analyze low level samples. The following procedure should be used:

9.1.5.1 Prepare a low level check sample by spiking 10 ul of QCcheck sample concentrated to 25 ml of reagent water and analyze according to the method in Section 10.0 .

9.1.5.2 For each analyte, the recovery must be between 60% and 140% of the expected value

9.1.5.3 When one or more analytes fail the test, the analyst must repeat the test only for those analytes which failed to meet the criteria. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs,locate

and correct the source of the problem and repeat the test for all compounds of interest beginning with 9.1.5.1.

9.1.6 The laboratory must maintain performance records to document the quality of data that is generated. The following procedure should be performed:

9.1.6.1 It is recommeded that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. As a minimum, field duplicate samples must be analyzed to assess the precision of the environmental measurements.

9.2 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations.

9.2.1 A quality control check sample concentrate containing each analyte at a concentration of 500 times the MDL in methanol is required. The QC check sample must be prepared by the laboratorry using stock standards prepared independently from those used for calibratio

9.2.2 Analyze seven 20-ml QC check samples at 2 ug/L according to the method beginning in Section 10.0 . Each sample is produced by injecting 10 ul of QC check sample concentrate into 25 ml of reagent water in a glass syringe through the syringe valve.

9.2.3 Calculate the average recovery (X) in ug/L, and the standard deviation of the recovery (S) in ug/L for each analyte using the seven results. Calculate the MDL for each analyte as specified in Reference 2. The calculated MDL must be less than the spike level.

9.2.4 For each analyte, (X) must be between 90% and 110% of the true value. Additionally, s must be <35% of X. If s and X for all analytes meet the criteria, the system performance is acceptable and analysis of actual samples can begin. If any s exceeds the precision limits or any X falls outside the range for accuracy, the system performance is unacceptable for that analyte.

NOTE: The larger number of analytes present a substantial probability that one or more will fail at least one of the acceptance criteria when all analytes are analyzed.

9.2.5 When one or more of the analytes tested fail at least one of the acceptance criteria, the analyst must proceed according to Section 9.2.2 only for the analytes which fialed the test.

10.0 PROCEDURE OF SAMPLE ANALYSIS

10.1 DAILY GC/MS PERFORMANCE TESTS

10.1.1 At the beginning of each day that analyses are to be performed, the GC/MS system must be checked to see if acceptable performance criteria are achieved for 4-Bromofluorobenzene (BFB). The performance test must be passed before any samples, blanks, or standard are analyzed.

10.1.2 At the beginning of each day, inject 2 ul (50 ng) of BFB solution directly onto the column. Alternatively, add 2 ul of BFB solution to 20.0 ml of reagent water or calibration standard and analyze the solution according to Section 8.1 Obtain a background-corrected mass spectrum of BFB and confirm that all the key m/z criteria in Table 4 are achieved. If all the criteria are not achieved, the analyst must re-tune the mass spectrometer and repeat the test until all criteria are achieved.

10.2 INITIAL CONDITIONS

10.2.1 Acquire GC/MS data for perfomance tests, standards and samples using the following instrumental conditions:

Electron Energy	:	70 V (Nominal)
Mass Range	:	35 to 300 amu
Scan Time	:	To give at least 5 scans per second, but not to exceed 2 seconds per scan.

10.2.1. The operating conditions for the gas chromatograph are summarized under Section 10.4.2.2 . Table 1 and Table 2 list the retention times and MDL that can be achieved under these conditions. Other columns or chromatographic conditions may be used if the requirements of Section 9.0 are met.

10.3 SAMPLE INTRODUCTION AND PURGING

10.3.1 Adjust the purge gas (nitrogen or helium) flow rate to 40 ml/min. Attach the trap inlet to the purging device and open the syringe valve on the purging device.

10.3.2 Remove the plungers from two 25-ml syringes and attach a closed syringe valve to each. Warm the sample to room temperature, open the sample (or standard) bottle, and carefully pour the sample into one of the syringe barrels to just short of overflowing. Replace the syringe plunger, invert the syringe, and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 20.0 ml. Add 10 ul of the internal standard spiking solution (Section 6.8) and 10 ul of the surrogate spiking standard solution (Section 6.9) to the sample through the syringe valve. Close the valve. Fill the second syringe in an identical manner from the same sample bottle. Reserve the second syringe for a reanalysis if necessary.

10.3.3 Attach the sample syringe valve to the syringe valve on the purging device. Be sure that the trap is cooler than 25_0C, then open the sample syringe valve and inject the sample into the purging chamber. Purge the sample for 11.0 ±0.1 min at ambient temperature.

10.4 SAMPLE DESORPTION

The mode of sample desorption is determined by the type of capillary column employed for the analysis. When using a wide-bore capillary column, follow the desorption conditions of Section 10.4.1 . The conditions for using narrow-bore capillary column is described in Section 10.4.

10.4.1 Sample Desorption for Wide-Bore Capillary Column

Undre most conditions,this type of column must be interfaced to MS through a all-glass jet separator

10.4.1.1 After the 11-minute purge, attach the trap to the chromatograph, adjust the purge and trap system to the desorb mode and initiate the temperature program sequence of the gas chromatograp and start data aquisition. Introduce the trapped materials to the GC column by rapidly heating the trap to 180°C while backflushing the trap with an iner gas at 15 ml/min for 4.0 ± 0.1 min. While the extracted sample is being introduced into the gas chromatograph, empty the purging device using the sampl syringe and wash the chamber with two 25-ml flushes of reagent water. After the purging device has been emptied, leave the syringe valve open to allow the purge gas to vent through the sample introduction needle.

10.4.1.2 Gas Chromatography - Hold the column temperature at 10°C for 5 minutes, then program at 6°C/min to 160°C and hold until all analytes eluted.

10.4.1.3 Trap Reconditioning - After desorbir the sample for 4 min, recondition the trap by returning the purge and trap system to the purge mode. Wait 15 seconds, then closed the syringe valve on the purging device to begin gas flow through the trap. Maintain the trap temperature at 180°C. After approximately 7 minutes, turn off the trap heater and open the syringe valve to stop the gas flow through the trap. When the trap is cool, the next sample can be analyzed.

10.4.2 Sample Desorption for Narrow-Bore Capillary Colum

Under normal operating conditions, most narrow-

bore capillary columns can be interfaced directly to the MS without a jet separator.

10.4.2.1 Sample Desorption

After the 11 minutes purge, attach the trap to the cyrogenically cooled interface at -15^{0}C and adjust the purge and trap system to the desorb mode. Introduce the trapped materials to the interface by rapidly heating the trap to 180^{0}C while backflusing the trap with an inert gas at 4 ml/min for 5.0+0.1 min. While the extracted sample is being introduced into the interface,empty the purging device using the sample syringe and rinse the chamber with two 25-ml flushes of reagent water. After the purging device has been emptied, leave the syringe valve open to allow the purge gas to vent through the sample introduction needle. After desorbing for 5 minutes, flash heat the interface to 250^{0}C and quickly introduce the sample onto the chromatographic column. Start the temperature program sequence, and initiate data acquisition.

10.4.2.2 Gas Chromatograph

Hold the column temperature at 10^{0}C for 5 minutes, then program at 6^{0}C/min to 70^{0}C and then at 15^{0}C/min to 145^{0}C.

10.4.2.3 Trap Reconditioning

After desorbing the sample for 5 minutes, recondition the trap by returning the purge and trap system to the purge mode. Wait 15 seconds, then close the syringe valve on the purging device to begin gas flow through the trap. Maintain the trap temperature at 180^{0}C. After approximately 15 minutes, turn off the trap heater and open the syringe valve to stop the gas

flow through the trap. When the trap is cool, the next sample can be analyzed

10.5 TERMINATION OF DATA ACQUISITION

When sample components have eluted from the GC, terminate MS data acquisition and store data files on the data syst storage device. Use appropriate data output software to display full range mass spectra and appropriate EICPs. *If any ion abundance exceeds the system working range,* dilute the sample aliquot in the second syringe with reagent water and analyze the diluted aliquot.

11.0 QUALITATIVE IDENTIFICATION

11.1 IDENTIFICATION PROCEDURES CRITERIA

Tentatively identify a sample component by comparison of its mass spectrum (after background substraction) to a reference spectrum in a collection. Use the follwoing criteria to confirm a tentative identification:

11.1.1 The GC retention time of the sample component must be within 10 seconds of the time observed for that sample compound when a calibration solution was analyzed.

11.1.2 All ions that are present above 10% relative abundance in the mass spectrum of the standard must be present in the mass spectrum of the sample component and should agree within absolute 10%. For example, if an ion has a relative abundance of 30% in the standard spectrum, its abundance in the sample component should be in the range of 20 to 40%.

11.1.3 Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. Because purgeable organic compounds are relatively small molecules and produce comparatively simple mass spectra, this is not a significant problem for most method analytes. When GC peaks obviously represent more than one sample component (i.e., broadened peak with shoulder(s) or valley between two or more

maxima), appropriate analyte spectra and background spectra can be selected by examining EICPs of characteriztic ions for tentatively identified components. When analytes coelute (i.e., only one GC peak is apparent), the identification criteria described in Section 11.1.2 can be met but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

11.1.4 Structural Isomers that produce very similar mass spectra can be explicity identified only if they have sufficiently different GC retention times. Acceptable resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

12.0 CALCULATION

12.1 When an analyte has been identified, the quantitation of that analyte should be based on the integrated abundance from the EICPs of the primary characteristic m/z given in Table 2. If the sample produces an interference for the primary m/z, use a secondary characteristic m/z to quantitate. Instrument calibration for secondary ions is performed, as necessary, using the data and procedures described in Section 8.2.

12.2 Calculate the concentration in the sample using the calibration curve or average response factor (RF) determined in Section 8.2.2 and Equation 3 :

$$\text{Concentration (ug/L)} = \frac{(A_S)\ (C_{IS})}{(A_{IS})\ (RF)} \qquad \text{Equ. 3}$$

Where,

A_S = Area of the characteristic m/z for the analyte to be measured;

A_{IS} = Area of the characteristic m/z for the internal standard;

C_{is} = Concentration of the internal standard, in ug/L.

12.3 Report results in ug/L. All QC data obtained should bereported with the sample results.

13.0 DATA REPROTING REQUIREMENTS

13.1 All reports and documentation must be legible, single-sided, and clearly labelled and paginated.

13.2 The sample data package must be consecutively paginated and shall include the cover pages, sample data, and the raw data as they are described in the following:

13.2.1 Cover Pages for the data package, including the project name; laboratory name; field sample number cross-referenced with laboratory ID number ; comments describing in details any problems encountered in processing the samples in the data package; and validation and signature by the Laboratry Manager.

13.2.2 Sample Data

Sample data shall be reported using the Organic Analysis Data Reporting Forms (Attachment I) for all samples, arranging in increasing alphanumeric sample number order, followed by the QC analysis data, Quarterly verification of instrument parameters forms, raw data, and copies of the sample preparation logs.

13.2.2.1 FORM I (Organic Analysis Data Sheet)

13.2.2.2 FORM I (Tentatively Identified Compounds

13.2.2.3 FORM II (Surrogate Recovery)

13.2.2.4 FORM III (Matrix Spike/Matrix Spike Duplicate Recovery)

13.2.2.5 FORM IV (Method Blank Summary)

13.2.2.6 FORM V (GC/MS Tuning and Mass

. Calibration)

13.2.2.7 FORM VI (Initial Calibration Data)

13.2.2.8 FORM VII (Continuing Calibration Data)

13.2.2.9 FORM VIII (Internal Standard Area Summary)

13.2.2.10 Raw Data

Raw data shall includes Reconstructed Ion Current (RIC) Chromatogram, Mass spectrum (with and without background substraction for all compounds quantified,mass spectrum of tentatively identified compound including the most matched library standard spectra, any instrument printouts, etc.

14.0 REFERENCES

14.1 A. Alford-Stevens, J.W. Eichelberger, W.L. Budde, "Purgeable Organic Compounds in Water by Gas Chromatography/Mass Spectrometry, Method 524." Environmental Monitoring and Support Laboratory, U.S. Environmental Protection Agency, Cincinnati, Ohio, February 1983.

14.2 Glaser, J. A., D. L. Foerst, G.D. McKee, S.A. Quave, and W.L.Budde, "Trace Analyses for Wastewaters," Environ. Sci. Technol., 15, 1426, 1981.

14.3 "The Determination of Halogenated Chemicals in Water by the Purge and Trap Method, Method 502.1, "Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, April, 1981.

14.4 "Volatile Aromatic and Unstaturated Organic Compounds in Water by Purge and Trap Gas Chromatography, Method 503.1," Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, April, 1981.

14.5 Bellar, T.A. and J.J. Lichtenberg, "The determination of Synthetic Organic Compounds in Water by Purge and Sequential Trapping Capillary Column Gas Chromatography," U.S.Environmental Protection Agency, Environmental

Monitoring and Support Laboratory, Cincinnati, Ohio,45268.

14.6 Ho. J.S. Method Performance Data for Method 502.2, Unpublished Report, September, 1986.

14.7 "Gas Chromatographic Analysis of Purgeable Halocarbon and Aromatic Compounds in Drinking Water Using Two Detectors in series," Kingsley, B.A., Gin, C., Coulson, D.M., and Thomas, R.F., Water Chlorination, Environmental Impact and Health Effects, Volume 4, Ann Arbor Science.

14.8 "EPA Method Validation Study 23, Method 601 (Purgeable Halocarbon)," U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268.

VOLATILE ORGANICS ANALYSIS DATA SHEET

Lab Name:_____

Field Sample Number_____.

Matrix: water Lab Sample ID: _____

Sample Vol: _____. mL Lab File ID: _____

Level: (low/med) _____ Date Received: _____

Date Analyzed: _____

Column: (pack/cap) _____ Dilution Factor: _____

CAS NO.	COMPOUND	CONCENTRATION UNITS: (ug/L	Q
74-87-3	Chloromethane		
74-83-9	Bromomethane		
75-01-4	Vinyl Chloride		
75-00-3	Chloroethane		
75-09-2	Methylene Chloride		
67-64-1	Acetone		
75-15-0	Carbon Disulfide		
75-35-4	1,1-Dichloroethene		
75-34-3	1,1-Dichloroethane		
540-59-0	1,2-Dichloroethene (total)		
67-66-3	Chloroform		
107-06-2	1,2-Dichloroethane		
78-93-3	2-Butanone		
71-55-6	1,1,1-Trichloroethane		
56-23-5	Carbon Tetrachloride		
108-05-4	Vinyl Acetate		
75-27-4	Bromodichloromethane		
78-87-5	1,2-Dichloropropane		
10061-01-5	cis-1,3-Dichloropropene		
79-01-6	Trichloroethene		
124-48-1	Dibromochloromethane		
79-00-5	1,1,2-Trichloroethane		
71-43-2	Benzene		
10061-02-6	trans-1,3-Dichloropropene		
75-25-2	Bromoform		
108-10-1	4-Methyl-2-Pentanone		
591-78-6	2-Hexanone		
127-18-4	Tetrachloroethene		
79-34-5	1,1,2,2-Tetrachloroethane		
108-88-3	Toluene		
108-90-7	Chlorobenzene		
100-41-4	Ethylbenzene		
100-42-5	Styrene		
1330-20-7	Xylene (total)		

VOLATILE ORGANICS ANALYSIS DATA SHEET
TENTATIVELY IDENTIFIED COMPOUNDS

Lab Name:_____

Lab Sample I.D. _____. Field Sample Number_____.

Matrix: water

Sample Vol: _____ mL Lab File ID: _____

Level: (low/med) _____ Date Received: _____

Date Analyzed: _____

Column: (pack/cap) _____ Dilution Factor: _____

Number TICs found: _____ CONCENTRATION UNITS: (ug/L

	CAS NUMBER	COMPOUND NAME	RT	EST. CONC.	Q
1.					
2.					
3.					
4.					
5.					
6.					
7.					
8.					
9.					
10.					
11.					
12.					
13.					
14.					
15.					
16.					
17.					
18.					
19.					
20.					
21.					
22.					
23.					
24.					
25.					
26.					
27.					
28.					
29.					
30.					

WATER VOLATILE SURROGATE RECOVERY

Lab Name: _____

	Field SAMPLE NO.	S1 (TOL) #	S2 (BFB) #	S3 (DCE) #	OTHER	TOT OUT
01						
02						
03						
04						
05						
06						
07						
08						
09						
10						
11						
12						
13						
14						
15						
16						
17						
18						
19						
20						
21						
22						
23						
24						
25						
26						
27						
28						
29						
30						

	QC LIMITS
S1 (TOL) = Toluene-d8	(88-110)
S2 (BFB) = Bromofluorobenzene	(86-115)
S3 (DCE) = 1,2-Dichloroethane-d4	(76-114)

Column to be used to flag recovery values

* Values outside of contract required QC limits

D Surrogates diluted out

WATER VOLATILE MATRIX SPIKE/MATRIX SPIKE DUPLICATE RECOVERY

Lab Name:_____

Lab Sample I.D. _____. Field Sample Number_____.

Matrix Spike - EPA Sample No.: _____

COMPOUND	SPIKE ADDED (ug/L)	SAMPLE CONCENTRATION (ug/L)	MS CONCENTRATION (ug/L)	MS % REC #	QC LIMITS REC.
1,1-Dichloroethene					61-145
Trichloroethene					71-12[illegible]
Benzene					76-12[illegible]
Toluene					76-125
Chlorobenzene					75-130

COMPOUND	SPIKE ADDED (ug/L)	MSD CONCENTRATION (ug/L)	MSD % REC #	% RPD #	QC LIMITS RPD	QC LIMITS REC.
1,1-Dichloroethene					14	61-145
Trichloroethene					14	71-120
Benzene					11	76-127
Toluene					13	76-12[illegible]
Chlorobenzene					13	75-13[illegible]

Column to be used to flag recovery and RPD values with an asterisk

* Values outside of QC limits

RPD:_____ out of _____ outside limits
Spike Recovery:_____ out of _____ outside limits

COMMENTS: _____

VOLATILE METHOD BLANK SUMMARY

Lab Name: _____

Lab File ID: _____ Lab Sample ID: _____

Date Analyzed: _____ Time Analyzed: _____

Matrix: water Level: (low/med) _____

Instrument ID: _____

THIS METHOD BLANK APPLIES TO THE FOLLOWING SAMPLES, MS AND MSD:

	Field SAMPLE NO.	LAB SAMPLE ID	LAB FILE ID	TIME ANALYZED
01				
02				
03				
04				
05				
06				
07				
08				
09				
10				
11				
12				
13				
14				
15				
16				
17				
18				
19				
20				
21				
22				
23				
24				
25				
26				
27				
28				
29				
30				

COMMENTS: _____

VOLATILE CONTINUING CALIBRATION CHECK

Lab Name:_____

Instrument ID: _____ Calibration Date:_____ Time:_____

Lab File ID: _____ Init. Calib. Date(s):_____ _____

Matrix: Water ___ Level:(low/med) _____ Column:(pack/cap) _____

Min RRF50 for SPCC(#) = 0.300 (0.250 for Bromoform) Max %D for CCC(*) = 25.0%

COMPOUND	RRF	RRF50	%D
Chloroethane			
Bromoethane			
Vinyl Chloride	*		*
Chloroethane			
Methylene Chloride			
Acetone			
Carbon Disulfide			
1,1-Dichloroethene	*		*
1,1-Dichloroethane	#		#
1,2-Dichloroethene (total)			
Chloroform	*		*
1,2-Dichloroethane			
2-Butanone			
1,1,1-Trichloroethane			
Carbon Tetrachloride			
Vinyl Acetate			
Bromodichloromethane			
1,2-Dichloropropane	*		*
cis-1,3-Dichloropropene			
Trichloroethene			
Dibromochloromethane			
1,1,2-Trichloroethane			
Benzene			
trans-1,3-Dichloropropene			
Bromoform	#		#
4-Methyl-2-Pentanone			
2-Hexanone			
Tetrachloroethene			
1,1,2,2-Tetrachloroethane	#		#
Toluene	*		*
Chlorobenzene	#		#
Ethylbenzene	*		*
Styrene			
Xylene (total)			
Toluene-d8			
Bromofluorobenzene			
1,2-Dichloroethane-d4			

VOLATILE ORGANIC GC/MS TUNING AND MASS CALIBRATION - BROMOFLUOROBENZENE (BFB)

Lab Name:_____

Lab Sample I.D. _____. Field Sample Number_____.

Lab File ID: _____ BFB Injection Date:_____

Instrument ID: _____ BFB Injection Time:_____

Matrix: (water/soil) _____ Level: (low/med) _____ Column: (pack/cap) _____

m/e	ION ABUNDANCE CRITERIA	% RELATIVE ABUNDANCE
50	15.0 - 40.0% of mass 95	
75	30.0 - 60.0% of mass 95	
95	Base peak, 100% relative abundance	
96	5.0 - 9.0% of mass 95	
173	Less than 2.0% of mass 174	( )1
174	Greater than 50.0% of mass 95	
175	5.0 - 9.0% of mass 174	( )1
176	Greater than 95.0%, but less than 101.0% of mass 174	( )1
177	5.0 - 9.0% of mass 176	( )2

1-Value is % mass 174 2-Value is % mass 176

THIS TUNE APPLIES TO THE FOLLOWING SAMPLES, MS, MSD, BLANKS, AND STANDARDS:

	Field SAMPLE NO.	LAB SAMPLE ID	LAB FILE ID	DATE ANALYZED	TIME ANALYZED
01					
02					
03					
04					
05					
06					
07					
08					
09					
10					
11					
12					
13					
14					
15					
16					
17					
18					
19					
20					
21					
22					

VOLATILE ORGANICS INITIAL CALIBRATION DATA

Lab Name:_____

Instrument ID: _____ Calibration Date(s):_____ _____

Matrix: water ___ Level:(low/med) _____ Column:(pack/cap) _____

Min $\overline{RRF}$ for SPCC(#) = 0.300 (0.250 for Bromoform) Max %RSD for CCC(*) = 30.0%

LAB FILE ID: RRF20 = _____ RRF50 = _____
RRF100= _____ RRF150= _____ RRF200= _____

COMPOUND	RRF20	RRF50	RRF100	RRF150	RRF200	$\overline{RRF}$	%RSD
Chloromethane*							
Bromomethane#							
Vinyl Chloride*							
Chloroethane							
Methylene Chloride*							
Acetone							
Carbon Disulfide							
1,1-Dichloroethene*							
1,1-Dichloroethane#							
1,2-Dichloroethene (total)*							
Chloroform*							
1,2-Dichloroethane#							
2-Butanone							
1,1,1-Trichloroethane#							
Carbon Tetrachloride#							
Vinyl Acetate							
Bromodichloromethane#							
1,2-Dichloropropane*							
cis-1,3-Dichloropropene*							
Trichloroethene*							
Dibromochloromethane#							
1,1,2-Trichloroethane#							
Benzene*							
trans-1,3-Dichloropropene*							
Bromoform#							
4-Methyl-2-Pentanone							
2-Hexanone							
Tetrachloroethene*							
1,1,2,2-Tetrachloroethane#							
Toluene*							
Chlorobenzene#							
Ethylbenzene*							
Styrene							
Xylene (total)							
Toluene-d8							
Bromofluorobenzene							
1,2-Dichloroethane-d4							

VOLATILE INTERNAL STANDARD AREA SUMMARY

Lab Name: _____

Lab File ID (Standard): _____ Date Analyzed: _____

Instrument ID: _____ Time Analyzed: _____

Matrix: Water ___ Level: (low/med) _____ Column: (pack/cap) _____

	IS1(BCM) AREA #	RT	IS2(DFB) AREA #	RT	IS3(CBZ) AREA #	RT
12 HOUR STD						
UPPER LIMIT						
LOWER LIMIT						
Field SAMPLE NO.						
01						
02						
03						
04						
05						
06						
07						
08						
09						
10						
11						
12						
13						
14						
15						
16						
17						
18						
19						
20						
21						
22						

IS1 (BCM) = Bromochloromethane
IS2 (DFB) = 1,4-Difluorobenzene
IS3 (CBZ) = Chlorobenzene-d5

UPPER LIMIT = + 100% of internal standard area.
LOWER LIMIT = - 50% of internal standard area.

Column used to flag internal standard area values with an asterisk

FORM VIII VOA

COVER PAGE - INORGANIC ANALYSES DATA PACKAGE

Lab Name: _____

Field Sample No.	Lab Sample ID.
_____	_____
_____	_____
_____	_____
_____	_____
_____	_____
_____	_____
_____	_____
_____	_____
_____	_____
_____	_____
_____	_____
_____	_____
_____	_____
_____	_____
_____	_____
_____	_____
_____	_____
_____	_____
_____	_____
_____	_____
_____	_____
_____	_____
_____	_____
_____	_____

Were ICP interelement corrections applied? Yes/No ___

Were ICP background corrections applied? Yes/No ___
If yes-were raw data generated before application of background corrections? Yes/No ___

Comments:

_____
_____
_____
_____

Release of the data contained in this hardcopy data package and in the computer-readable data submitted on floppy diskette has been authorized by the Laboratory Manager or the Manager's designee, as verified by the following signature.

Lab Manager: _____

Date: _____

Semi-Volatile Organics

STANDARD OPERATING PROCEDURE

FOR

THE ANALYSIS OF SEMIVOLATILE ORGANICS IN DRINKING WATER WITH LOW DETECTION LIMITS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY

PREPARED
by

Cheng-Wen Tsai

December, 1988

STANDARD OPERATING PROCEDURE

The Analysis of Semivolatile Organics in Drinking Water With Low Detection Limits By Gas Chromatography/Mass Spectrometry

1.0 SCOPE AND APPLICATION

This method covers the analysis of the semivolatile organics listed in TABLE 1 in drinking water (private well/municiple well) samples using gas chromatography/mass spectrometry (GC/MS). The required method detection limits of this method is lower than that of the standard GC/MS scan of semivolatile organics. Modifications are made to achieve these low detection limits. The level of surrogate spike standard and matrix spike standard are proportionatel reduced.

2.0 SUMMARY OF METHOD

2.1 Two separate one liter aliquots of sample are extracted with methylene chloride at a pH greater than 11 for base/neutral fractions and again at pH less than 2 for acid fraction, using separataory funnel techniques.

2.2 For each aliquot of sample, the acid fraction and the base/neutral fractions are combined and concentrated down to 0.5 ml. This concentrated extract is then analyzed using a GC/MS system. The analytes of interest, which are separated by GC, are measured by a mass spectrometer detector in the electron impact (EC) mode.

2.3 The retention time and mass spectra are the criteria of qualitative identification of analytes. The quantitation ions used for quantifying each analyte are listed in TABLE 2.

3.0 SAFETY PRECAUTIONS

3.1 The toxicity or carcinogenicity of chemicals used in this method have not been precisely defined. Each

TABLE 1

TARGET COMPOUND LIST (TCL) AND QUANTITATION LIMITS (ug/L)

(FOR RESIDENTIAL WELL WATER SAMPLES)

SEMIVOLATILES	CAS NUMBER	QUANTITATION LIMITS
Bis(2-chloroethyl) ether	111-44-4	1.5
Phenol	108-95-2	2.0
2-Chlorophenol	95-57-8	2.0
1,3-Dichlorobenzene	541-73-1	2.0
1,4-Dichlorobenzene	106-46-7	2.0
1,2-Dichlorobenzene	95-50-1	2.5
Benzyl Alcohol	100-51-6	2.0
Bis(2-chloroisopropyl) ether	39638-32-9	2.5
2-Methyl Phenol	95-48-7	1.0
Hexachloroethane	67-72-1	2.0
N-Nitrosodipropylamine	621-64-7	1.5
Nitrobenzene	98-95-3	2.5
4-Methylphenol	106-44-5	1.0
Isophorone	78-59-1	2.5
2-Nitrophenol	88-75-5	2.0
2,4-Dimethylphenol	105-57-9	2.0
Bis(2-chloroethoxyl) Methane	111-91-1	2.5
2,4-Dichlorophenol	120-83-2	2.0
1,24-Trichlorobenzene	120-82-1	2.0
Naphthalene	91-20-3	2.0
4-Chloroaniline	106-47-8	2.0
Hexachlorobutadiene	87-68-3	2.5
Benzoic Acid	65-85-0	20.0
2-Methyl Naphthalene	91-57-6	2.0
4-Chloro-3-Methylphenol	59-50-7	1.5
Hexachlorocyclopentadiene	77-47-4	2.0
2,4,6-Trichlorophenol	88-06-2	1.5
2,4,5-Trichlorophenol	95-95-4	1.5
2-Chloro Naphthalene	91-58-7	1.5
Acenaphthylene	208-96-8	1.5
Dimethyl Phthalate	131-11-3	1.5
2,6-Dinitrotoluene	606-20-2	1.0
Acenaphthene	83-32-9	1.5
3-Nitroaniline	99-09-2	2.5
Dibenzofuran	132-64-9	1.0
2,4-Dinitrophenol	51-28-5	(15.0)
2,4-Dinitrotoluene	121-14-2	1.0

NOTE: Values in parenthesis are estimated.

TABLE 2

CHARACTERISTIC IONS FOR SEMIVOLATILE ORGANICS PARAMETERS

Parameter	Primary Ion	Secondary Ion(s)
Phenol	94	65, 66
Bis(2-chloroethyl)Ether	93	63, 95
2-Chlorophenol	128	64, 130
1,3-Dichlorobenzene	146	148, 113
1,4-Dichlorobenzene	146	148, 113
Benzyl Alcohol	108	79, 77
1,2-Dichlorobenzene	146	148, 113
2-Methylphenol	108	107
Bis(2-chloroisopropyl)Ether	45	77, 79
4-Methylphenol	108	107
N-Nitroso-Dipropylamine	70	42, 101, 130
Hexachloroethane	117	201, 199
Nitrobenzene	77	123, 65
Isophorone	82	95, 138
2-Nitrophenol	139	65, 109
2,4-Dimethylphenol	107	121, 122
Benzoic Acid	122	105, 77
Bis(2-Chloroethoxy)Methane	93	95, 123
2,4-Dichlorophenol	162	164, 98
1,2,4-Trichlorobenzene	180	182, 145
Naphthalene	128	129, 127
4-Chloroaniline	127	129
Hexachlorobutadiene	225	223, 227
4-Chloro-3-Methylphenol	107	144, 142
2-Methylnaphthalene	142	141
Hexachlorocyclopentadiene	237	235, 272
2,4,6-Trichlorophenol	196	198, 200
2,4,5-Trichlorophenol	196	198, 200
2-Chloronaphthalene	162	164, 127
2-Nitroaniline	65	92, 138
Dimethyl Phthalate	163	194, 164
Acenaphthylene	152	151, 153
3-Nitroaniline	138	108, 92
Acenaphthene	153	152, 154
2,4-Dinitrophenol	184	63, 154
4-Nitrophenol	109	139, 65
Dibenzofuran	168	139
2,4-Dinitrotoluene	165	63, 182
2,6-Dinitrotoluene	165	89, 121
Diethylphthalate	149	177, 150

4-chlorophenyl-phenylether	204	206, 142
Fluorene	166	165, 167
4-Nitroaniline	138	92, 108
4,6-Dinitro-2-Methylphenol	198	182, 77
N-Nitrosodiphenylamine	169	168, 167
4-Bromophenyl-phenylether	248	250, 141
Hexachlorobenzene	284	142, 249
Pentachlorophenol	266	264, 268
Phenanthrene	178	179, 176
Anthracene	178	179, 176
Di-n-Butylphthalate	149	150, 104
Fluoranthene	202	101, 100
Pyrene	202	101, 100
Butylbenzylphthalate	149	91, 206
3,3-Dichlorobenzidine	252	254, 126
Benzo(a)anthracene	228	229, 226
Bis(2-Ethylhexyl)phthalate	149	167, 279
Chrysene	228	226, 229
Di-n-Octyl phthalate	149	-
Benzo(b)Fluoranthene	252	253, 125
Benzo(k)Fluoranthene	252	253, 125
Benzo(a)Pyrene	252	253, 125
Indeno(1,2,3-cd)Pyrene	276	138, 227
Dibenz(a,h)Anthracene	278	139, 279
Benzo(g,h,i)Perylene	276	138, 277

chemical shall be treated as potential health hazard and exposure to these chemicals should be minimized. Each analyst is responsible for maintaining awareness of OSHA regulations regarding safe handling of chemicals used in this method. Additional references to laboratory safety are available for the information of the analyst.

3.2 The following parameters covered by this method have been tentatively classified as known or suspected, human or mammalian carcinogens : Benzo(a)anthracene, benzidine, 3,3-dichlorobenzidine, benzo(a)pyrene, dibenzo(a,h) anthracene, and N-nitrosodimethylamine. Primary standards of these toxic compounds should be prepared in a well-vented hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

4.0 INTERFERENCES

4.1 Method interferences may be caused by contaminants in reagents,solvents, glassware, and other samples processing hardware, that lead to discrete artifacts or elevated baselines in the total ion current profiles (TICPs). All of these materials must be routinely demonstrated to be free of interferences under the conditions of the analysis by running laboratory reagent blanks.

4.2 Matrix interferences may be caused by contaminants that coextracted from the sample. The extent of matrix interferences will vary considerably from sample to sample. Matrix spike/matrix spike duplicate (MS/MSD) analyses will be done to determine the possible matrix interferences.

5.0 APPARATUR AND INSTRUMENTS

5.1 Glassware

5.1.1 Separatory funnel - 2000 ml, with teflon stopper.

5.1.2 Drying column - 19 mm ID chromatographic column with coarse frit.

5.1.3 Concentrator tube - Kuderna-Danish, 10 ml,

graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked at the volume employed in the test. Ground glass stopper is used to prevent evaporation of extracts.

5.1.4 Evaporative flask - Kuderna-Danish, 500 ml (Kontes K-503000-0500 or equivalent). Attach to concentrator tube with springs.

5.1.5 Snyder column - Kuderna-Danish, Three-ball macro (Kontes K-503000-0121 or equivalent).

5.1.6 Snyder column - Kuderna-Danish, two-ball micro (Knotes K-50300-0219 or equivalent).

5.1.7 Vials - amber glass, 2 ml capacity with teflon-lined screw-cap.

5.1.8 Continuous liquid-liquid extractors - equiped with teflon or glass connecting joints and stopcocks requiring no lubrication.

5.1.9 Silicon carbide boiling chips - approximately 10/40 mesh. Heat to 400 degree C for 30 minutes or Soxhlet extract with methylene chloride.

5.2 Balance - analytical, capable of accurately weighing +0.00001 g.

5.3 Water bath - heated, with concentric ring cover, capable of temperature control ($+2^{0}C$). The bath should be used in a hood.

5.4 Nitrogen evaporation device equipped with a water bath that can be maintained at a temperature between 35 and $40^{0}C$.

5.5 Gas chromatography/mass spectrometer system

5.5.1 Gas chromatography - an analytical system complete with a temperature programmable gas chromatograph suitable for splitless injection, and all required accessories including syringes, analytical columns, and carrier gases.

5.5.2 GC columns - 30 m x 0.25 mm (or 0.32 mm) ID bonded-phase silicon coated fused silica caillary column (J&W Scientific DB-5 or

equivalent). A film thickness of 1.0 micro is recommended because of its larger capacity. Alternately, a film thickness of 0.25 micro may be used.

5.5.3 Mass spectrometer - capable of scanning from 35 to 500 amu every 1 second or less, utilizing 70 volts (nominal) electron energy in the electron impact ionization mode and producing a mass spectrum which meets all criteria when 50 ng of decafluorotriphenyl-phosphine (DFTPP) is injected through the GC inlet.

5.5.4 Data system - a computer system must be interfaced to the mass spectrometer that allows the continuous acquisition and storage on machine readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have a library of standard mass spectra, and have software that allows library search of mass spectra in both forward and reversed mode, searching of any GC/MS file for ions of a specific mass and plotting such ion abundance versus time or scan number. This type of plot is defined as an extracted ion current profile (EICP). Software must also be available that allows integrating the abundance in any EICP between specified time or scan number limits.

6.0 REAGENTS

6.1 Reagent water - reagent water is defined as a water in which an interferent is not observed at or above the method detection limit of each parameter of interest.

6.2 Sodium hydroxide solution (10 N) - dissolve 40 g analytical grade NaOH in reagent water and dilute to 100 ml.

6.3 Sodium thiosulfate - (ACS) granular.

6.4 Sulfuric acid solution (1+1) - slowly add 50 ml concentrated H_2SO_4 (sp.gr. 1.84) to 50 ml of reagent water.

6.5 Acetone and methanol - pesticide residue analysis grade

or equivalent quality.

6.6 Sodium sulfate - (ACS) powdered, anhydrous. purified by heating at 400°C for four hours in a shallow tray, cool in a desicator, and store in a glass botle.

6.7 Methylene Chloride - Pesticide residue analysis grade or equivalent.

6.8 Surrogate standard spike solution

6.8.1 Surrogate standards are added to all investigative samples, matrix spike/matrix spike duplicate samples, laboratory duplicate samples,blanks and calibration standard slutions. The surrogate standard spiking solution should include the following compounds:

Nitrobenzene-d_5	Phenol-d_6
Terphenyl-d_{14}	2,4,6-tribromophenol
2-fluorobiphenyl	2-fluorophenol

6.8.2 Prepare a surrogate standard spike solution that contains the base/neutral compounds at a concentration of 20 ug/ml, and the acid compounds at 40 ug/ml. Store the spike solutions at 4°C in teflon-sealed containers. The solution should be checked frequently for stability. These solutions must be replaced after three months or sooner if comparison with quality control check samples indicate a problem.

6.9 Base/Neutral and Acid Matrix Standard Spiking Solution

6.9.1 The matrix standard spiking solution should consist of the following compounds:

Base/Neutrals	Acids
1,2,4-Trichlorobenzene	Pentachlorophenol
Acenaphthene	Phenol
2,4-Dinitrophenol	2-Chlorophenol
Pyrene	4-Chloro-4-Methylphenol
N-Nitroso-di-n-propylamine	4-Nitrophenol
1,4-Dichlorobenzene	

6.9.2 Prepare a spiking solution in methanol that contains all of the compounds in 6.8.1 at a concentration of 20 ug/ml for base/neutrals, and at 40 ug/mL for acids. Store the spiking solutions at 4^0C ($+2^0C$) in Teflon-sealed containers. The solutions shall be checked frequently for stability. These solutions shall be replaced after twelve months, or sooner, if comparison with quality control check samples indicates a problem.

6.10 Internal Standards

6.10.1 The internal standard solution consists of the following compounds:

1,4-dichlorobenzene-d_4	Naphthalene-d_8
Acenaphthene-d_{10}	Phenanthrene-d_{10}
Chrysene-d_{12}	Perylene-d_{12}

6.10.2 Prepare the internal standard solution by dissolving 200 mg of each compound in 50 ml of methylene chloride. It may be necessary, however, to use 5-10% benzene or toluene in this solution and a few minutes of ultresonic mixing to dissolve all the constitutes. The resulting solution will contain each standard compound at a concentration of 4000 ng/ml. A 10 ul portion of this solution should be added to 1 ml of sample extract (or 5 ul to 0.5 ml extract). This will give a concentration of 40 ng/ul of each compound.

6.11 Calibration standard solution

6.11.1 Initial Calibration standard solutions -

Prepare calibration standard solutions at a minimum of five concentration levels. Each calibration standard solution shall contain each compound of interest and each surrogate standard. The concentration of the initial calibration standard solutions shall be at 5, 10, 20 50, and 100 ng/uL (or mg/L) for all semivolatiles except the following compounds: Benzoic acid, 2,4-dinitrophenol, 2,4,5-trichlorophenol, 4,6-dinitro-2-methylphenol, 4-nitrophenol, pentachlorophenol, and all three iosmers of nitroaniline, which

will have concentrations at 20, 50, 80, , and 120 ng/ul (or mg/L).

Great care must be taken to maintain the integrity of all standard solutions. Store all standard solutions at -10°C to -20°C in screw-cap amber bottles with teflon liners. Fresh standards shall be prepared every twelve months at a minimum. The continuing calibration standard shall be prepared weekly and stored at 4°C (+2°C),.

6.11.2 Continuing Calibration Check Standard solution -

Prepare a continuing calibrtation check standard solution at a concentration of 20 ng/uL for all base/neutral and acids compounds except benzoic acid, 2,4,5-trichlorophenol, 4,6-dinitro-2-methylphenol, 4-nitrophenol, pentachlorophenol and three isomers of nitroaniline, which will be at a concentration of 40 ng/uL. The continuing calibration check standard solution shall contain each surrogate standard.

7.0 PROCEDURES

7.1 Sample Storage and Holding Time

7.1.1 Procedure for Sample Storage

7.1.1.1 The samples must be protected from light and refrigerrated at 4°C from the time of receipt until sample extraction and analysis.

7.1.2 Holding Time

7.1.2.1 The extraction of water samples should be completed within 5 days VSTR (validated time of sample receipt.)

7.2 Sample Extraction - Separatory Funnel

7.2.1 Two separate one liter of water samples will be extracted respectively using the separatory funnel.The extraction scheme is described as below.

7.2.1.1 Place entire sample of one liter bottle into a 2-liter separatory funnel (Note: if the liter bottle is not completely filled, mark the sample level on the outside of the bottle so that the volume of sample used for extraction can be measured later by filling it with reagent water.). Rinse the bottle and cap with reagent water, and add it to the sample.

7.2.1.2 Add 250 ul of surrogate standard spiking solution into the separatory funnel and mix it well. (For matrix spike samples, add 250 ul of matrix spiking solution to each 1-liter portion of sample.) Check the pH of the sample with wide range pH paper and adjust it to pH greater than 11 with 10 N sodium hydroxide.

7.2.1.3 Add 60 ml of methylene chloride to the separatory funnel and extract the sample by shaking the funnel for 2 minutes, with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface between layers is more than one-third of the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends on the sample, and may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. Collect the methylene chloride extract in a 250 ml Erlenmeyer flask.

7.2.1.4 Add a second 60-ml portion of methylene chloride to the sample in the separatory funnel and repeat the extraction procedure a second time, combining the extracts in

the erlenmeyer flask. Perform a third extraction in the same maaner. Combine the extracts in the erlenmeyer flask, and label the combined extract as the base/neutral fraction. Continue the extraction for acid fraction in 7.2.5 .

7.2.1.5 Adjust the pH of the aqueous phase to less than 2 using sulfuric acid (1-1). Serially extract three times with 60-ml aliquots of methylene chloride, as per 7.2.3 through 7.2.4 . Collect and combine the extracts in a 250 ml erlenmeyer flask and label the combined extract as the acid fraction.

7.2.1.6 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-ml concentrator tube to a 500-ml evaporative flask.

7.2.1.7 Transfer the individual base/neutral and acid fractions by pouring extracts through separate drying column containing about 10 cm of anhydrous granular sodium sulfate, and collect the extracts in the separate K-D concentrators. Rinse the erlenmeyer flasks and columns with 20 to 30 ml of methylene chloride to complete the quantitative transfer.

7.2.1.8 Add one or two clean boiling chips and attach a three-ball snyder column to the evaporative flask. Pre-wet the snyder column by adding about 1 ml methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (80^0 to 90^0C) so that the concentrator tube is partially immersed in the hot water, and the entire lower round surface of the flask is bathed with hot water vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 10 to 15 minutes. At the proper rate of distillation, the ball of the column will actively chatter but the chambers

will not flood with condensed solvent. When the apparent volume of liquid reaches 1 ml, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes. Remove the snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 ml of methylene chloride. A 5-ml syringe is recommended for this operation.

7.2.1.9 Nitrogen blowdown

Place the concentrator tube in a warm water bath (35°C) and evaporate the solvent volume to just below 1 ml using a gentle stream of clean, dry nitrogen filtered through a column of active carbon.
Caution: New plastic tubing must NOT be used between the carbon trap and the sample, as it may introduce interferences. The internal wall of the tube must be rinsed down several times with methylene chloride during the operation and the final volume brought to 0.5 ml with methylene chloride. During evaporation, the tube solvent level must be kept below the water level of the bath. The extract must never be allowed to become dry.

7.3 Tuning and GC/MS Mass Calibration

7.3.1 It is necessary to establish that a given GC/MS meets the standard mass spectral abundance criteria before initiating any on-going data collection. This is accomplished through the hardware tuning and the analysis of decafluorotriphenylphosphine (DFTPP).

7.3.1.1 Each GC/MS system used for the analysis of semivolatile compounds must be hardware-tuned to meet the abundance criteria listed in TABLE 3 for a 50-ng injection of DFTPP.

DFTPP must be analyzed separately or

TABLE 3

CHARACTERISTIC IONS FOR SURROGATE AND INTERNAL STANDARDS FOR SEMIVOLATILE ORGANIC COMPOUNDS

Parameters	Primary Ion	Secondary Ions
SURROAGES		
Phenol-d_5	99	42, 71
2-Fluorophenol	112	64
2,4,6-Tribromophenol	330	332, 141
Nitrobenzene-d_5	82	128, 54
2-Fluorobiphenyl	172	171
Terphenyl	244	122, 212
INTERNAL STANDARDS		
1,4-Dichlorobenzene-d_4	152	115
Naphthalene-d_8	136	68
Acenaphthene-d_{10}	164	162, 160
Phenanthrene-d_{10}	188	94, 80
Chrysene-d_{12}	240	120, 236
Perylene-d_{12}	264	260, 265

as part of the calibration standard. The meeting the criteria of abundance must be demonstrated daily and/or for each 12 hour period, whichever is more frequent, before samples can be analyzed. DFTPP must injected to meet this criteria.

7.3.1.2 Whenever corrective action is taken that may change or affect the tuning criteria for DFTPP (e.g., ion source cleaning or repair, etc.), the tune must be verified irrespective of the 12-hour tuning requirements.

Table 4. DFTPP Key Ions and Ion Abundance Criteria

Mass	Ion Abundance Criteria
51	30.0 - 60.% of mass 198
68	Less than 2.0% of mass 69
70	Less than 2.0% of mass 69
127	40.0 - 60.0% of mass 198
197	Less than 1.0% of mass 198
198	Base peak, 100% relative abundance
199	5.0 - 9.0% of mass 198
275	10.0 - 30.0% of mass 198
365	Greater than 1.0% of mass 198
441	Present, but less than mass 443
442	Greater than 40.0% of mass 198
443	17.0 - 23.0% of mass 442

7.3.2 Calibration of the GC/MS System

7.3.2.1 Before the analysis of samples and required blanks, and after tuning criteria have been met, the GC/MS system must be initially calibrated as a minimum of five concentrations to determine the linearity of response utilizing all compounds listed in Table 1. Once the system has been calibrated, the calibration must be verified after initial calibration

and after every 12-hour time period for each GC/MS system.

7.3.2.2 Prepare calibration standards to yield the following specific concentrations:

Initial calibration of semivolatile compounds consists of five points at 5, 10, 20, 50, and 100 total nanograms for all compounds except for the folllowing compounds:

Benzoic acid, 2,4-dinitrophenol, 2,4,5-trichlorophenol, 4,6-dinitro-2-methylphenol, 4-nitrophenol, pentachlorophenol, and all three nitroaniline isomers which will be injected at 20,50, 80,and 120 total nanograms.

7.3.2.3 Analyze each calibration standard and tabulate the area of the primary characterizitc ion (Table 2) against concentration for each compound including all required surrogate and internal standard compounds. The relative retention times of each compound in each calibration run should agree within 0.06 retention time units. Late eluting compounds usually will have much better agreement.

The relative response factors (RRFs) for each compound at each concentration level are calculated using Equation 1.

$$RRF = \frac{(A_x) \times (C_{is})}{(A_{is}) \times (C_x)} \qquad \text{Equ. 1}$$

Where:

A_x = Area of the characteristic ion for the compound to be measured.

A_{is} = Area of the characteristic ion for the specific internal standards from Table 2 or 3.

C_{is} = Concentration of the internal standard in uint of ng/uL.

C_x = Concentration of the compound to be measured in unit of ng/uL.

Using the relative response factors (RRFs) from the initial calibration, and Equation 2 to calculate the percent relative standard deviation (%RSD) for each compound from the calibration check run.

$$\%RSD = \frac{SD}{X} \times 100 \qquad \text{Equ. 2}$$

Where:

%RSD = Relative Standard Deviation

SD = Standard Deviation of initial response factors per each compound.

Where: $$SD = \sum_{i=1}^{N} \frac{(Xi - X)}{N - 1}$$

X = mean of initial response factors per each compound.

The %RSD for each individual compound must be less than or equal to 25%. This criteria must be met for the initial calibration to be valid, and the sequencial continuing calibration check

7.4 GC/MS Analysis of Sample

7.4.1 The follwoing instrumental parameters are required for all performance tests and for all sample analysis:

Electron Energy - 70 volts (nominal)

Mass Range - 35 to 500 amu

Scan Time - 1 second per scan

7.4.2 Combine 0.5 ml of the base/neutral extract and 0.5 ml of acid from water extract prior to analysis.

7.4.3 Internal standard solution is added to each sample extract. Add 10 ul of internal standard solution (6.10) to each accurately measured 1.0 ml of combined sample extract (or 5 ul of internal standard solution to 0.5 ml of base/neutral extract or 0.5 ml of acid extract respectively).

7.4.4 Analyze the 1.0 ml combined extract by GC/MS using a bonded-phase silicone-coated fused silica capillary column. The recommended GC operating conditions to be used are as follows:

Initial Column Temperature Hold- 30^0C for 4 minutes

Column Temperature Program - 30-300^0C at 8 degree/min.

Final Column Temperature Hold - 300^0C for 10 min.

Injector Temperature - 250 - 300^0C

Transfer Line Temperature - 250 - 300^0C

Source Temperature - According to manufacturer's specification.

Injector-Grob-Type, Splitless

Sample Volume - 1 - 2 uL

Carrier Gas - Helium at 30 cm/sec

NOTE: Make any extract dilution indicated by characterization prior to the addition of

internal standards. If any further dilution of water extracts are made, additional internal standards must be added to maintain the required 40 ng/uL of each constituent in the extract volume. If the concentration of any compound exceeds the initial calibration range, the extract must be diluted and reanalyzed. Secondary ion quantitation is **ONLY** allowed when there are sample interferences with the primary ion.

7.5 Qualitative Analysis

7.5.1 The compounds listed in Table 1 shall be identified by an analyst competent in the interpretation of mass spectra by comparison of the sample mass spectrum to the mass spectrum of a standard of the suspected compound. The following criteria must be satisfied in order to verifythe identifications: (1) elution of the sample component at the GC relative retention time as the standard component, and (2) correspondence of the sample component and standard component mass spectra.

7.5.1.1 For establinshing correspondence of the GC relative retention time (RRT), the sample component RRT must compare within +0.06 RRT units of the RRT of the standard component. For reference, the standard must be run on the same shift as the sample. If coelution of interfering components prohibits accurate assignment of the sample component RRT from the total ion chromatogram, the RRT should be assigned by using extracted ion current profiles for ions unique to the component of interest.

7.5.1.2 For comparison of standard and sample component mass spectra, mass spectra obtained on the same GC/MS instrument are required. Once obtained, these standard spectra may be used for identification purposes, only if

analysis, follow the instruction in Section 10.1 regarding dilution of extracts and reporting results.

11.0 CALCULATION

11.1 Determine the concentrationof individual compounds in the sample.

11.1.1 If the external standard calibration procedure used, calculate the amount of material injected from the peak response using the calibration curve or calibration factor determined in Section 7.2.2. The concentration in the sample can be calculated from the following equation:

$$\text{Concentration (ug/L)} = \frac{(A)\ (V_t)}{(V_i)\ (V_s)}$$

Where:

A = Amount of material injected (ng).

V_i = Volume of extract injected (ul).

V_t = Volume of total extract (ul)

V_s = Volume of water sample extacted (ml)

12.0 DATA REPORTING REQUIREMENT

12.1 All reports and documentations shall be legible, single-sided, and clearly labelled and paginated.

12.2 The sample data package shall be consecutively paginated, and shall include cover pages, sample data, raw data.

12.2.1 Cover pages for the data package, including the project name, laboratory name, field sample number cross-referenced with laboratory ID number, comments describing in details any problems encountered in processing the samples,

all confirmation standards for a case or set at the beginning, at intervals of every 5 samples, and at the end. Any pesticide outside the retention time window requires immediate investigation and correction before continue the analysis. The laboratory shall reanalyze all samples between the standard that exceeds the criteria and a subsequent standard that meet the criteria.

10.2.6 Begin injection of samples. Analyze group of 5 samples with a standard pertaining to the sample after each group (Evaluation Standard Mix B is required after the first 5 samples, and every 10 samples thereafter).
The alternating standard calibration factors must be within 15.0%of each other if quantitation is performed. Deviation greater than 15% requires the laboratory to repeat the samples analyzed between the standrad that exceeds the criteria and a subsequent standard that meet the criteria. The 15% criteria only pertains to compounds being quantitated.

10.2.6.1 If more than one standard is required to confirm all compounds identified in the primary analysis, includes a alternate standard after each 10 samples.

10.2.6.2 Samples shall also be repested if the degradation of either DDT and/or endrin exceed 20% on the intermitten Evaluation Standard Mix B.

10.2.6.3 If the sample s are splitted between 2 or more instruments, all standards and blanks pertaining to those samples must be analyzed on each instruments.

10.2.7 Inject the method blank (extract with each set of 20 samples) on every GC and GC columns on which the samples are analyzed.

10.2.8 If quantitation is performed on the confirmation

the GC/MS instrument meets the DFTPP daily tuning requirements. These spectra may be obtained from the run used to obtain reference RRTs.

7.5.1.3 The requirements for qualitative verification by comparison of mass spectra are as follows:

7.5.1.3.1 All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) must be present in the sample spectrum.

7.5.1.3.2 The relative intensities of ions specified in (1) must agree within plus or minus 20% between the standard and sample spectra.

7.5.1.3.3 Ions greater than 10% in the sample spectrum but not present in the standard spectrum must be considered and accounted for by the analyst making the comparison. All compounds meeting the identification criteria must be reported with their spectra. For all compounds below the CRDL, report the actual value followed by "J", e.g., "3J."

7.5.1.3.4 If a compound can not be verified by all of the criteria in 7.5.1.3.3, but in the technical judgement of the mass spectral interpreatation specialist, the identification is correct, then the laboratory shall report that identification and proceed with quantitation.

7.6 Tentative Identification of Non-target compound/Unknown

Sample components.

A library search shall be executed for non-target compounds or unknown sample components for the purpose of tentative identification.The 1985 release of the National Bureau of Standards Mass Spectral Library or the most current release shall be used for this purpose.

7.6.1 Substances with responses equal to, or greater than 10% of the nearest internal standard are required to be searched in this fashion. Only after visual comparison of sample spectra with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification. **NOTE: Computer generated library search routines must not use normalization routines that would misrepresent the library or unknown spectra when compared to each other.**

7.6.2 The following criteria shall be used to make the tentative identification:

7.6.2.1 Relative intensities of major ions in the reference spectrum (ions greater than 10% of the most abundant ion) should be present in the sample spectra.

7.6.2.2. The relative intensities of the major ions should agree within +20% .

7.6.2.3 Molecular ions present in reference spectrum should be present in sample spectrum.

7.6.2.4 Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of co-eluting compounds.

7.6.2.5 Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible substraction from the sample spectrum because of background contamination or co-eluting compounds. **NOTE: Data system library reduction programs can sometimes create these discrepancies.**

7.6.2.6 If in the technical judgement of the mass interpreatation spectral specialist, no valid tentative identification can be made, the compound shall be reported as Unknown. The mass spectral specialist should give additional classification of the unknown compound, if possible (i.e., unknown phthalate, unknown hydrocarbon, unknown acid type, unknown chlorinated compound, etc.). If probale molecular weights can be distinguished, include them.

7.7 Quantitation

7.7.1 Components identified shall be quantified by the internal standard method. The internal standard used shall be the one nearest the retention time to that of a given analyte. The EICP area of the characteristic ions of analytes listed in Table 2 and Table 3 are used.

Internal standard responses and retention time in all samples must be evaluated during or immediately after data acquisition. If the retention time for any internal standard changes by more than 30 seconds from the latest daily (12 hour) calibration standard, the charomatographic system must be inspected for malfunctions, and corrections made as required. The extracted ion current profile (EICP) of the internal standards must be monitored and evaluated for each sample, blank, matrix spike, and matrix spike duplicate. If the EICP area for any internal standard changes by more than a factor of two (-50% to +100%), the mass spectrometric system must be inspected for malfunction and corrections made as appropriate. If the analyses of a subsequent sample or standard indicates that the system is functioning properly, the corrections may not be required. The sample or standards with EICP areas outside the limits must be re-analyzed, and treated according to 7.7.1.1 and 7.7.1.2 below. If correction is made, then the laboratory must demonstrate that the mass spectrometric system is functioning properly. This must be accompanied bythe analysis of a standard or sample that does

meet the EICP criteria. After corrections are made, the re-analysis of samples analyzed while the system was malfunctioning is required.

7.7.1.1 If after re-analysis, the EICP areas for all internal standards are inside the required limits (-50% to +100%), then the problem with the first analysis is considered to have been within the control of laboraotry. There only data from the analysis with EICP's within the required limits will be reported.

7.7.1.2 If the re-analysis of the sample does not solve the problem(i.e., the EICP areas are outside the required limits for both analyses), then the EICP data and sample data from both analyses shall be reported. Distinguish between the initial analysis and the re-analysis on all data deliverables. Document in the case narrative all inspection and corrective action taken.

7.7.2 The relative response factor (RRF) from the daily standard analysis is used to calculate the concentration in the sample. Secondary ions may be used if interferences are present. The area of a secondardy ion can **NOT** be substituted for the area of a primary ion unless a relative response factor is calculated using the secondary ion. When compounds identified are below required quantitation limits (RQL) but the spectral meets the identification criteria, report the concentration with a "J." See Section 8.0 for calculation.

8.0 CALCULATION

8.1 When an analyte has been identified, the quantitation of that analyte shall be based on the integrated abundance from the EICPs of the primary characteristic ion given in Table 2. If the sample produces an interference for the primary ion, use a secondary characteriztic ion for quantitation. Instrument calibration for secondary ions shall be performed, as necessary, using the data and procedures described in Section 7.0.

8.2 Calculate the concentration in the sample using the calibration curve or relative response factor (RRF) as determined in Section 7.3.2.3, and the following equation:

$$\text{Concentration (ug/L)} = \frac{(A_x)\ (I_s)\ (V_t)}{(A_{is})\ (RRF)\ (V_o)\ (V_i)}$$

Where A_x = Area of the characteristic ion for the compound to be measured.

A_{is} = Area of the characteristic ion for the internal standard.

I_s = Amount of internal standard injected in nanograms (ng).

V_o = Volume of water extracted in milliliter (ml)

V_i = Volume of extract injected (ul)

V_t = Volume of total extract (use 2000 ul or a factor of this when dilutions are made. The 2000 ul is derived from combining half of the 1 ml BN extract and half of the 1 ml of A extract.)

8.3 Estimation of Tentatively Identified Compounds (TICs)

An estimated concentration for the non-target components tentatively identified shall be quantified by the internal standard method. For quantification, the nearest internal standard free of interferences shall be used.

8.3.1 The equation for calculating concentrations is the same as in Section 12.2 . Total area counts (or peak heights) from the total ion chromatogams are to be used for both the compound to be measured and the internal standard. A relative response factor (RRF) of one (1) is to be assumed. The value from this quantitation shall be qualified as estimated. This estimated concentration shall be calculated for all tentatively identified compounds as well as those identified as unknowns.

8.4 Calculate surrogate standard recovery on all samples, blanks and spike samples. Detemine if recovery is within limits and report on appropriate form. The surrogate standard recovery for each sample, blank, and spike samples are calculated as following:

$$\text{Surrogate Standard Recovery} = \frac{SSR}{SA} \times 10$$

Where:

SSR = Surrogate spike sample result.

SA = Surrogate standard spike added from surrogate spike mix.

8.5 Matrix Spike/Matrix Spike Duplicate Analysis (MS/MSD

8.5.1 Individual component recoveries of the matrix spike are calculated using the following equations:

$$\text{Marix Spike Percent Recovery} = \frac{SSR - SR}{SA} \times 100$$

Where:

SSR = Spike sample results.

SR = Spike result.

SA = Spike added from spiking mix.

8.5.2 Relative Percent Difference (RPD)

The relative percent difference for each component between the matrix spike and matrix spike duplicate are calculated using the following equation:

$$RPD = \frac{D_1 - D_2}{((D_1) + (D_2))/2} \times 100$$

Where:

RPD = Relative percent difference.

D_1 = First sample value.

D_2 = Second sample value (duplicate)

9.0 QUALITY CONTROL REQUIREMENTS

9.1 The continuing calibration check shall be done daily before analysis of any samples, and once at the beginning of each 12-hour shift to check the validity of the initial calibration. Calculate the percent difference (%D) using the following equation:

$$\% \text{ Difference} = \frac{RF_I - RF_C}{RF_I} \times 100$$

Where:

RF_I = Average response factor from initial calibration.

RF_C = Response factor from current continuing

calibration check standard.

The percent difference for any compound shall be less than 25%. If the criteria is not met (>25% difference), for anyone calibration check compound, corrective action **must** be taken. If no source of the problem can be determined after corrective action has been taken, a new initial five point calibration must be generated. This criteria **must** be met before sample analysis begins.

9.2 Method Blank Analysis

9.2.1 A method blank is a volume of deionized,distilled laboratory water carried through the entire analytical scheme (extraction, concentration, and analysis). The method blank volume shall be approximately equal to the sample volumes being processed.

9.2.2 The method blank analysis shall be performed at a frequency of one per group of 20 of fewer samples of similar concentration. The method blank associated with a specific group of samples shall be analyzed on each GC/MS system used to analyze that specific group of samples.

9.2.3 A method blank shall contain no greater than five times (5X) the required detection limit of common phthalate esters, and shall contain less than the required detection limit of any other single semi-volatile compounds. If the method blank exceeds this criteria, the source of contamination must be investigated, and appropriate corrective measures must be taken and documented before further sample analysis proceeds. All samples processed with a method blank that is out of control must be reextracted and reanalyzed.

9.3 Surrogate Spike Recovery

9.3.1 Calculate surrogate spike percent recovery per Section 8.4. Surrogate spike recovery shall be evaluated for acceptance by determining whether the concentration (measured as percent recovery) falls inside the required recovery limits listed as follows:

SURROGATE SPIKE RECOVERY LIMITS

Surrogate Compound	Low/Medium Water
Nitrobenzene-d_5	35-114
2-Fluorobiphenyl	43-116
p-Terphenyl-d_{14}	33-141
Phenol-d_5	10-94
2-Fluorophenol	21-100
2,4,6-Tribromophenol	10-123

9.3.2 If recovery of any one surrogate compound in either base/neutral or acid fraction is below 10% or recoveries of two surrogate compounds in either base/neutral or acid fraction are outside the surrogate spike recovery limits (9.3.1), corrective actions shall be taken. If no source of problems is determined after the corrective actions are taken, reextract and reanalyze the sample.

9.4 Matrix Spike/Matrix Spike Duplicate Analysis (MS/MSD)

9.4.1 A matrix spike/matrix spike duplicate shall be performed one per group of 20 or fewer samples of similar concentrations.

9.4.2 The matrix spike percent recovery shall be calculated according to Section 8.5. The matrix spike recovery limits are listed as below:

Matrix Spike Recovery Limits

Fraction	Matrix Spike Compound	Limits

BN	1,2,4-Trichlorobenzene	39-98
BN	Acenaphthene	46-118
BN	2,4-dinitrotoluene	24-96
BN	Pyrene	26-127
BN	N-Nitroso-Di-Propylamine	41-116
BN	1,4-Dichlorobenzene	36-97
Acid	Pentachlorophenol	9-103
Acid	Phenol	12-89
Acid	2-Chlorophenol	27-123
Acid	4-chloro-3-Methylphenol	23-97
Acid	4-Nitrophenol	10-80

9.5 Sample Analysis

9.5.1 Sample can ONLY be analyzed upon successful completion of the initial QC activities (7.3, 9.1, 9.2, 9.3 and 9.5). When twelve (12) hours have elapsed since the initial QC was completed, it is necessary to conduct an instrument tune and calibration check analysis. Any major system maintenance such as source cleaning or installation of a new column, may necessitate a retune and recalibration.

9.5.2 Requirements for qualitative compound identification and quantitation specified in 7.5 and 7.6 shall be followed.

10.0 DATA REPORTING REQUIREMENT

10.1 All reports and documentations shall be legible, single-sided, and clearly labelled and paginated.

10.2 The sample data package shall be consecutively paginated and shall include the cover pages, sample data, and the raw data as they are described in the following:

10.2.1 Cover pages for the data package, including the project name, laboratory name, field

sample number cross-referenced with laboratory ID number, comments describing in details any problems encountered in processing the samples, and validation and signature by the Laboratory Manager.

10.2.2 Sample Data

Sample data shall be reported using the Organic Analysis Data Reporting Forms (Attachment I) for all samples, arranging in increasing alphanumeric sample number order, followed by QC analyses data, Quarterly verification of instrument parameters forms, raw data including copies of the sample custody and sample preparation logs.

10.2.2.1 FORM IA (Semivolatile Organics Analyses Data Sheet)

FORM IB (Semivolatile Organics Analysis Data Sheet - continued)

FORM IC (Semivolatile Organics Analysis Data Sheet - Tentatively Identified Compounds, TICs)

10.2.2.2 FORM II (Semivolatile Surrogate Recovery)

10.2.2.3 FORM III (Semivolatile Matrix Spike Matrix Spike Duplicate Recovery)

10.2.2.4 FORM IV (Semivolatile Method Blank Recovery)

10.2.2.5 FORM V (Semivolatile GC/MS Tuning and Mass Calibration - Decafluorotriphenylphosphine (DFTPP))

10.2.2.6 FORM VI (Semivolatile Initial Calibration Data)

10.2.2.7 FORM VII (Semivolatile Continuing Calibration Check Data)

10.2.2.8 FORM VIII (Semivolatile Internal Standard Area Summary)

10.2.2.9 Raw Data

Raw data shall include reconstructed Ion currect (RIC) chromatogram, mass spectra (with and without background substraction) of each compound quantified, mass spectrum of each tentatively identified compound (TIC) including the best matched standard library spectrum, any instrument printouts, copies of sample custody records and sample preparation logs.

11.0 REFERENCES

SEMIVOLATILE ORGANICS ANALYSIS DATA SHEET

Lab Name:_____

Lab Sample I.D. _____. Field Sample Number_____.

Matrix: water — Lab Sample ID: _____

Sample vol: _____ mL — Lab File ID: _____

Level: (low/med) _____ — Date Received: _____

Date Extracted:_____

Extraction: (SepF/Cont/Sonc) _____ — Date Analyzed: _____

GPC Cleanup: (Y/N)___ pH:____ — Dilution Factor: _____

CAS NO.	COMPOUND	CONCENTRATION UNITS: (ug/L	Q
108-95-2	Phenol		
111-44-4	bis(2-Chloroethyl)ether		
95-57-8	2-Chlorophenol		
541-73-1	1,3-Dichlorobenzene		
106-46-7	1,4-Dichlorobenzene		
100-51-6	Benzyl alcohol		
95-50-1	1,2-Dichlorobenzene		
95-48-7	2-Methylphenol		
108-60-1	bis(2-Chloroisopropyl)ether		
106-44-5	4-Methylphenol		
621-64-7	N-Nitroso-di-n-propylamine		
67-72-1	Hexachloroethane		
98-95-3	Nitrobenzene		
78-59-1	Isophorone		
88-75-5	2-Nitrophenol		
105-67-9	2,4-Dimethylphenol		
65-85-0	Benzoic acid		
111-91-1	bis(2-Chloroethoxy)methane		
120-83-2	2,4-Dichlorophenol		
120-82-1	1,2,4-Trichlorobenzene		
91-20-3	Naphthalene		
106-47-8	4-Chloroaniline		
87-68-3	Hexachlorobutadiene		
59-50-7	4-Chloro-3-methylphenol		
91-57-6	2-Methylnaphthalene		
77-47-4	Hexachlorocyclopentadiene		
88-06-2	2,4,6-Trichlorophenol		
95-95-4	2,4,5-Trichlorophenol		
91-58-7	2-Chloronaphthalene		
88-74-4	2-Nitroaniline		
131-11-3	Dimethylphthalate		
208-96-8	Acenaphthylene		
606-20-2	2,6-Dinitrotoluene		

SEMIVOLATILE ORGANICS ANALYSIS DATA SHEET

Lab Name:_____

Lab Sample I.D. _____. Field Sample Number_____.

Matrix: water — Lab Sample ID: _____

Sample vol: _____ ml — Lab File ID: _____

Level: (low/med) _____ — Date Received: _____

Date Extracted:_____

Extraction: (SepF/Cont/Sonc) _____ — Date Analyzed: _____

GPC Cleanup: (Y/N)___ pH:___ — Dilution Factor: _____

CAS NO.	COMPOUND	CONCENTRATION UNITS: (ug/L	Q
99-09-2	3-Nitroaniline		
83-32-9	Acenaphthene		
51-28-5	2,4-Dinitrophenol		
100-02-7	4-Nitrophenol		
132-64-9	Dibenzofuran		
121-14-2	2,4-Dinitrotoluene		
84-66-2	Diethylphthalate		
7005-72-3	4-Chlorophenyl-phenylether		
86-73-7	Fluorene		
100-01-6	4-Nitroaniline		
534-52-1	4,6-Dinitro-2-methylphenol		
86-30-6	N-Nitrosodiphenylamine (1)		
101-55-3	4-Bromophenyl-phenylether		
118-74-1	Hexachlorobenzene		
87-86-5	Pentachlorophenol		
85-01-8	Phenanthrene		
120-12-7	Anthracene		
84-74-2	Di-n-butylphthalate		
206-44-0	Fluoranthene		
129-00-0	Pyrene		
85-68-7	Butylbenzylphthalate		
91-94-1	3,3'-Dichlorobenzidine		
56-55-3	Benzo(a)anthracene		
218-01-9	Chrysene		
117-81-7	bis(2-Ethylhexyl)phthalate		
117-84-0	Di-n-octylphthalate		
205-99-2	Benzo(b)fluoranthene		
207-08-9	Benzo(k)fluoranthene		
50-32-8	Benzo(a)pyrene		
193-39-5	Indeno(1,2,3-cd)pyrene		
53-70-3	Dibenz(a,h)anthracene		
191-24-2	Benzo(g,h,i)perylene		

(1) - Cannot be separated from Diphenylamine

SEMIVOLATILE ORGANICS ANALYSIS DATA SHEET
TENTATIVELY IDENTIFIED COMPOUNDS

Lab Name: _____

Field Sample number _____.

Matrix: water — Lab Sample ID: _____

Sample vol: _____ mL — Lab File ID: _____

Level: (low/med) _____ — Date Received: _____

% Moisture: not dec._____ dec._____ — Date Extracted:_____

Extraction: (SepF/Cont/Sonc) _____ — Date Analyzed: _____

GPC Cleanup: (Y/N)___ pH:___ — Dilution Factor: _____

Number TICs found: _____

CONCENTRATION UNITS:
(ug/L

CAS NUMBER	COMPOUND NAME	RT	EST. CONC.	Q
1.				
2.				
3.				
4.				
5.				
6.				
7.				
8.				
9.				
10.				
11.				
12.				
13.				
14.				
15.				
16.				
17.				
18.				
19.				
20.				
21.				
22.				
23.				
24.				
25.				
26.				
27.				
28.				
29.				
30.				

WATER SEMIVOLATILE SURROGATE RECOVERY

Lab Name: _____

	Field SAMPLE NO.	S1 (NBZ) #	S2 (FBP) #	S3 (TPH) #	S4 (PHL) #	S5 (2FP) #	S6 (TBP) #	OTHER	TOT OUT
01									
02									
03									
04									
05									
06									
07									
08									
09									
10									
11									
12									
13									
14									
15									
16									
17									
18									
19									
20									
21									
22									
23									
24									
25									
26									
27									
28									
29									
30									

		QC LIMITS
S1 (NBZ)	= Nitrobenzene-d5	(35-114)
S2 (FBP)	= 2-Fluorobiphenyl	(43-116)
S3 (TPH)	= Terphenyl-d14	(33-141)
S4 (PHL)	= Phenol-d6	(10-94)
S5 (2FP)	= 2-Fluorophenol	(21-100)
S6 (TBP)	= 2,4,6-Tribromophenol	(10-123)

Column to be used to flag recovery values
* Values outside of contract required QC limits
D Surrogates diluted out

WATER SEMIVOLATILE MATRIX SPIKE/MATRIX SPIKE DUPLICATE RECOVERY

Lab Name:_____

Lab Sample I.D. _____. Field Sample Number_____.

Matrix Spike - EPA Sample No.: _____

COMPOUND	SPIKE ADDED (ug/L)	SAMPLE CONCENTRATION (ug/L)	MS CONCENTRATION (ug/L)	MS % REC #	QC LIMITS REC.
Phenol					12- 89
2-Chlorophenol					27-123
1,4-Dichlorobenzene					36- 97
N-Nitroso-di-n-prop.(1)					41-116
1,2,4-Trichlorobenzene					39- 98
4-Chloro-3-methylphenol					23- [illegible]
Acenaphthene					46-118
4-Nitrophenol					10- 80
2,4-Dinitrotoluene					24- 96
Pentachlorophenol					9-103
Pyrene					26-127

COMPOUND	SPIKE ADDED (ug/L)	MSD CONCENTRATION (ug/L)	MSD % REC #	% RPD #	QC LIMITS RPD	QC LIMITS REC.
Phenol					42	12- 89
2-Chlorophenol					40	27-123
1,4-Dichlorobenzene					28	36- 97
N-Nitroso-di-n-prop.(1)					38	41-116
1,2,4-Trichlorobenzene					28	39- 98
4-Chloro-3-methylphenol					42	23- 97
Acenaphthene					31	46-118
4-Nitrophenol					50	10- 80
2,4-Dinitrotoluene					38	24- 96
Pentachlorophenol					50	9-103
Pyrene					31	26-127

(1) N-Nitroso-di-n-propylamine

Column to be used to flag recovery and RPD values with an asterisk
* Values outside of QC limits

RPD:_____ out of _____ outside limits
Spike Recovery:_____ out of _____ outside limits

COMMENTS: _____

_____

SEMIVOLATILE METHOD BLANK SUMMARY

Lab Name: _____

Lab File ID: _____ Lab Sample ID: _____

Date Extracted: _____ Extraction: (SepF/Cont/Sonc) ____

Date Analyzed: _____ Time Analyzed: _____

Matrix: water Level: (low/med) ____

Instrument ID: _____

THIS METHOD BLANK APPLIES TO THE FOLLOWING SAMPLES, MS AND MSD:

	Field SAMPLE NO.	LAB SAMPLE ID	LAB FILE ID	DATE ANALYZED
01				
02				
03				
04				
05				
06				
07				
08				
09				
10				
11				
12				
13				
14				
15				
16				
17				
18				
19				
20				
21				
22				
23				
24				
25				
26				
27				
28				
29				
30				

COMMENTS: _____

SEMIVOLATILE ORGANIC GC/MS TUNING AND MASS CALIBRATION - DECAFLUOROTRIPHENYLPHOSPHINE (DFTPP)

Lab Name:_____

Lab File ID: _____ DFTPP Injection Date:_____

Instrument ID: _____ DFTPP Injection Time:_____

m/e	ION ABUNDANCE CRITERIA	% RELATIVE ABUNDANCE
51	30.0 - 60.0% of mass 198	
68	Less than 2.0% of mass 69	( )1
69	Mass 69 relative abundance	
70	Less than 2.0% of mass 69	( )1
127	40.0 - 60.0% of mass 198	
197	Less than 1.0% of mass 198	
198	Base Peak, 100% relative abundance	
199	5.0 to 9.0% of mass 198	
275	10.0 - 30.0% of mass 198	
365	Greater than 1.00% of mass 198	
441	Present, but less than mass 443	
442	Greater than 40.0% of mass 198	
443	17.0 - 23.0% of mass 442	( )2

1-Value is % mass 69 2-Value is % mass 442

THIS TUNE APPLIES TO THE FOLLOWING SAMPLES, MS, MSD, BLANKS, AND STANDARDS:

	Field SAMPLE NO.	LAB SAMPLE ID	LAB FILE ID	DATE ANALYZED	TIME ANALYZED
01					
02					
03					
04					
05					
06					
07					
08					
09					
10					
11					
12					
13					
14					
15					
16					
17					
18					
19					
20					
21					
22					

SEMIVOLATILE ORGANICS INITIAL CALIBRATION DATA

Lab Name: _____

Instrument ID: _____ Calibration Date(s): _____ _____

Min $\overline{RRF}$ for SPCC(#) = 0.050 Max %RSD for CCC(*) = 30.0%

LAB FILE ID: RRF20 = _____ RRF50 = _____
RRF80 = _____ RRF120 = _____ RRF160 = _____

COMPOUND	RRF20	RRF50	RRF80	RRF120	RRF160	$\overline{RRF}$	%RSD
Phenol*							
bis(2-Chloroethyl)ether							
2-Chlorophenol							
1,3-Dichlorobenzene							
1,4-Dichlorobenzene*							
Benzyl alcohol							
1,2-Dichlorobenzene							
2-Methylphenol							
bis(2-Chloroisopropyl)ether							
4-Methylphenol							
N-Nitroso-di-n-propylamine*							
Hexachloroethane							
Nitrobenzene							
Isophorone							
2-Nitrophenol*							
2,4-Dimethylphenol							
Benzoic acid							
bis(2-Chloroethoxy)methane							
2,4-Dichlorophenol*							
1,2,4-Trichlorobenzene							
Naphthalene							
4-Chloroaniline							
Hexachlorobutadiene*							
4-Chloro-3-methylphenol*							
2-Methylnaphthalene							
Hexachlorocyclopentadiene*							
2,4,6-Trichlorophenol*							
2,4,5-Trichlorophenol							
2-Chloronaphthalene							
2-Nitroaniline							
Dimethylphthalate							
Acenaphthylene							
2,6-Dinitrotoluene							
3-Nitroaniline							
Acenaphthene*							
2,4-Dinitrophenol#							
4-Nitrophenol#							

VOLATILE ORGANICS INITIAL CALIBRATION DATA

Lab Name:_____

Instrument ID: _____ Calibration Date(s):_____ _____

Min $\overline{RRF}$ for SPCC(#) = 0.050 Max %RSD for CCC(*) = 30.0%

LAB FILE ID: RRF20 =_____ RRF50 =_____
RRF80 =_____ RRF120=_____ RRF160=_____

COMPOUND	RRF20	RRF50	RRF80	RRF120	RRF160	$\overline{RRF}$	%RSD
Dibenzofuran							
2,4-Dinitrotoluene							
Diethylphthalate							
4-Chlorophenyl-phenylether							
Fluorene							
4-Nitroaniline							
4,6-Dinitro-2-methylphenol							
N-Nitrosodiphenylamine (1)	*						*
4-Bromophenyl-phenylether							
Hexachlorobenzene							
Pentachlorophenol	*						*
Phenanthrene							
Anthracene							
Di-n-butylphthalate							
Fluoranthene	*						*
Pyrene							
Butylbenzylphthalate							
3,3'-Dichlorobenzidine							
Benzo(a)anthracene							
Chrysene							
bis(2-Ethylhexyl)phthalate							
Di-n-octylphthalate	*						*
Benzo(b)fluoranthene							
Benzo(k)fluoranthene							
Benzo(a)pyrene	*						*
Indeno(1,2,3-cd)pyrene							
Dibenz(a,h)anthracene							
Benzo(g,h,i)perylene							
Nitrobenzene-d5							
2-Fluorobiphenyl							
Terphenyl-d14							
Phenol-d6							
2-Fluorophenol							
2,4,6-Tribromophenol							

(1) Cannot be separated from Diphenylamine

SEMIVOLATILE CONTINUING CALIBRATION CHECK

Lab Name:_____

Instrument ID: _____ Calibration Date:_____ Time:_____

Lab File ID: _____ Init. Calib. Date(s):_____ _____

Min RRF50 for SPCC(#) = 0.050 Max %D for CCC(*) = 25.0%

COMPOUND	$\overline{RRF}$	RRF50	%D
Phenol*			*
bis(2-Chloroethyl)ether			
2-Chlorophenol			
1,3-Dichlorobenzene			
1,4-Dichlorobenzene*			*
Benzyl alcohol			
1,2-Dichlorobenzene			
2-Methylphenol			
bis(2-Chloroisopropyl)ether			
4-Methylphenol			
N-Nitroso-di-n-propylamine#			#
Hexachloroethane			
Nitrobenzene			
Isophorone			
2-Nitrophenol*			*
2,4-Dimethylphenol			
Benzoic acid			
bis(2-Chloroethoxy)methane			
2,4-Dichlorophenol*			*
1,2,4-Trichlorobenzene			
Naphthalene			
4-Chloroaniline			
Hexachlorobutadiene#			#
4-Chloro-3-methylphenol*			*
2-Methylnaphthalene			
Hexachlorocyclopentadiene#			#
2,4,6-Trichlorophenol*			*
2,4,5-Trichlorophenol			
2-Chloronaphthalene			
2-Nitroaniline			
Dimethylphthalate			
Acenaphthylene			
2,6-Dinitrotoluene			
3-Nitroaniline			
Acenaphthene*			*
2,4-Dinitrophenol#			#
4-Nitrophenol#			#

SEMIVOLATILE CONTINUING CALIBRATION CHECK

Lab Name:_____

Instrument ID: _____ Calibration Date:_____ Time:_____

Lab File ID: _____ Init. Calib. Date(s):_____ _____

Min RRF50 for SPCC(#) = 0.050 Max %D for CCC(*) = 25.0%

COMPOUND	$\overline{RRF}$	RRF50	%D
Dibenzofuran			
2,4-Dinitrotoluene			
Diethylphthalate			
4-Chlorophenyl-phenylether			
Fluorene			
4-Nitroaniline			
4,6-Dinitro-2-methylphenol			
N-Nitrosodiphenylamine (1) *			*
4-Bromophenyl-phenylether			
Hexachlorobenzene			
Pentachlorophenol *			*
Phenanthrene			
Anthracene			
Di-n-butylphthalate			
Fluoranthene *			*
Pyrene			
Butylbenzylphthalate			
3,3'-Dichlorobenzidine			
Benzo(a)anthracene			
Chrysene			
bis(2-Ethylhexyl)phthalate			
Di-n-octylphthalate *			*
Benzo(b)fluoranthene			
Benzo(k)fluoranthene			
Benzo(a)pyrene *			*
Indeno(1,2,3-cd)pyrene			
Dibenz(a,h)anthracene			
Benzo(g,h,i)perylene			
Nitrobenzene-d5			
2-Fluorobiphenyl			
Terphenyl-d14			
Phenol-d6			
2-Fluorophenol			
2,4,6-Tribromophenol			

(1) Cannot be separated from Diphenylamine

SEMIVOLATILE INTERNAL STANDARD AREA SUMMARY

Lab Name: _____

Lab File ID (Standard): _____ Date Analyzed: _____

Instrument ID: _____ Time Analyzed: _____

	IS1(DCB) AREA #	RT	IS2(NPT) AREA #	RT	IS3(ANT) AREA #	RT
12 HOUR STD						
UPPER LIMIT						
LOWER LIMIT						
Field SAMPLE NO.						
01						
02						
03						
04						
05						
06						
07						
08						
09						
10						
11						
12						
13						
14						
15						
16						
17						
18						
19						
20						
21						
22						

IS1 (DCB) = 1,4-Dichlorobenzene-d4
IS2 (NPT) = Naphthalene-d8
IS3 (ANT) = Acenaphthene-d10

UPPER LIMIT = + 100% of internal standard area.
LOWER LIMIT = - 50% of internal standard area.

Column used to flag internal standard area values with an asterisk

SEMIVOLATILE INTERNAL STANDARD AREA SUMMARY

Lab Name: _____

Lab File ID (Standard): _____ Date Analyzed: _____

Instrument ID: _____ Time Analyzed: _____

	IS4(PHN) AREA #	RT	IS5(CRY) AREA #	RT	IS6(PRY) AREA #	RT
12 HOUR STD						
UPPER LIMIT						
LOWER LIMIT						
Field SAMPLE NO.						
01						
02						
03						
04						
05						
06						
07						
08						
09						
10						
11						
12						
13						
14						
15						
16						
17						
18						
19						
20						
21						
22						

IS4 (PHN) = Phenanthrene-d10
IS5 (CRY) = Chrysene-d12
IS6 (PRY) = Perylene-d12

UPPER LIMIT = + 100% of internal standard area.
LOWER LIMIT = - 50% of internal standard area.

Column used to flag internal standard area values with an asterisk

Pesticides/PCBs

STANDARD OPERATING PROCEDURE

FOR

THE ANALYSIS OF PESTICIDES/PCBs IN WATER WITH LOW DETECTION LIMITS

PREPARED BY

Cheng-Wen Tsai

July 6, 1988

Revised January, 1989

STANDARD OPERATING PROCEDURE

FOR

THE ANALYSIS OF PESTICIDES AND PCBs IN DRINKING WATERS

1.0 INTRODUCTION

1.1 This standard operating procedure describe the detailed analytical procedure for the determination of organochlorine pesticides and polychlorinated biphenyl (PCBs) listed in Table 1 in private well water, domestic well and municipal water samples.

1.2 This is a gas chromatography with electron capture detection (GC-EC). This method also describes analytical conditions for a second gas chromatographic column that shall be used to confirm measurements made with the primary column.

1.3 The method detection limits (MDLs) for each parameter is listed in Table 1.

1.4 This method is restricted to use by or under the supervision of analysts experienced in the use of a gas chromatograph and in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Section .

2.0 SUMMARY OF METHOD

2.1 A 1-liter sample is extracted with methylene chloride using a separatory funnel. The methylene chloride extract is dried with anhydrous sodium sulfate and exchanged to hexane during the concentration to a volume of 1 ml. The extract is separated by gas chromatography and the parameters are then measured with an electron capture detector (ECD).

2.2 This method provides a florisil column cleanup procedure and an elemental sulfur removal procedure to aid in the elimination of interference that may be encountered.

TABLE 1

TARGET COMPOUND LIST (TCL) AND QUANTITATION LIMITS (QL)

(For Residential Well Water Samples)

Pesticides/PCBs	CAS Number	Quantitation Limits (ug/L)
alpha-BHC	319-84-6	0.010
Beta-BHC	319-85-7	0.005
delta-BHC	319-86-8	0.005
Gamma-BHC (Lindane)	58-89-9	0.005
Heptachlor	76-44-8	0.030
Aldrin	309-00-2	0.005
Heptachlor epoxide	1024-57-3	0.005
Endosulfan I	959-98-8	0.010
Dieldrin	60-57-1	0.010
4,4'-DDE	72-55-9	0.005
Endrin	72-20-8	0.010
Endosulfan II	33213-65-9	0.010
4,4'-DDD	72-54-8	0.020
Endosulfan Sulfate	1031-07-8	0.100
4,4'-DDT	50-29-3	0.020
Methoxychlor	72-43-5	0.020
Endrin Ketone	53494-70-5	0.030
alpha-chlordane	5103-71-9	0.020
gamma-chlordane	5103-74-2	0.020
Toxaphene	8001-35-2	0.250
Aroclor-1016	12674-11-2	0.100
Aroclor-1221	11104-28-2	0.100
Aroclor-1232	11141-16-5	0.100
Aroclor-1242	53469-21-9	0.100
Aroclor 1248	12672-29-6	0.100
Aroclor-1254	11097-69-1	0.100
Aroclor-1260	11096-82-5	0.100

3.0 INTERFERENCES

3.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks (Section 8.2). The use of high purity reagents and solvents help to minimize interference problem.

3.2 Glassware must be scrupulously cleaned. Clean all glassware as soon as possible after use by rinsing with the last solvent used in it. Solvent rinsing should be followed by detergent washing with hot water, and rinses with tap water The glassware shall then be drained dry, and heated in a muffle furnace at 400^{0}C for 15 to 30 minutes.

3.3 Interferences by phthalate esters can pose a major problem in pesticide analysis when using the electron capture detector. These compounds generally appear in the chromatogram as large late eluting peaks, especially in the 15 and 50% fractions from florisil. Interferences from phthalates can best be minimized by avoiding the use of plastics in the laboratory. Exhaustive cleanup of reagents and glassware may be required to elimiate background phthalate contamination.

3.4 Matrix interferences may be caused by by contaminants that are co-extracted from the sample. The cleanup procedure in Section 9.4 shall be used to overcome many of these interferences.

4.0 SAFETY PRECAUTIONS

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. Exposure to the chemicals therefore must be reduced to the lowest possibel level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets shall also be made available to all

personnel involved in the chemical analysis.

4.2 The following parameters covered by this method have been tentatively classified as known or suspected, human or mammalian carcinogens: 4,4'-DDT, 4,4'-DDD, the BHCs, and the PCBs. Primary standards of these toxic compounds should be prepared in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

5.0 APPARATUS AND MATERIALS

5.1 Sampling Equipment

5.1.1 Grab sample bottle - 1-liter amber bottle, fritted with a screw cap lined with Teflon. The bottle and cap liner must be washed, rinsed with acetone or methylene chloride, and dried before they are shipped to field to minimize contamination.

5.2 Glasswares

5.2.1 Separatory Funnel - 2-liters with Teflon stopcock.

5.2.2 Drying column - Chromatographic column, approximately 400 mm long x 19 mm ID., with coarse frit filter disc.

5.2.3 Chromatographic Column - 400 mm long x 22 mm ID, with Teflon stopcock and corse frit filter disc.

5.2.4 Concentrator tube, Kuderna-Danish - 10-ml, graduated. Ground glass stopper is used to prevent evaporation of extracts.

5.2.5 Evaporative Flask, Kuderna-Danish - 500-ml. Attached to concentrator tube with springs.

5.2.6 Snyder column, Kuderna/Danish - Three balls macro.

5.2.7 Vials - 10 to 15 ml amber glass, with Teflon-lined screw cap.

5.3 Boiling chips - approximately 10/40 mesh. Heat to 400^{0}C for 30 minutes or soxhlet extract with

methylene chloride.

5.4 Water Bath - Heated, with concentric ring cover, capable of temperature control (+2^{0}C). The bath shall be used in a hood.

5.5 Balance - Analytical, capable of accurately wieghing 0.0001 g.

5.6 Gas Chromatograph - an analytical system complete with gas chromatograph suitable for on-column injection and all required accessories including syringes, analytical columns, gases, detector, and strip chart recorder. A data system is recommended for measuring peak areas.

5.6.1 Quantitation and/or confirmation columns:

5.6.1.1 GC Column 1 - 1.8 m long x 4 mm ID glass packed with 1.5% SP-2250 / 1.95% SP-2401 on Supelcoport (100/120 mesh) or equivalent.

5.6.1.2 GC Column 2 - 1.8 m long x 4 mm ID, glass, packed with 3% OV-1 on Supelcoport(100/120 mesh) or equivalent.

5.6.1.3 GC Column 3 - 1.8 m long x 4 mm ID, glass, packed with 5% OV-210 on Gas Chrom Q (80/100 mesh) or equivalent.

5.6.2 Confirmation column ONLY :

Column - 30 m x 0.25 mm ID, 0.25 micron film thickness, bonded-phase silicone coated, fused silica capillary column (J&W Scientific DB-5 or DB-1701 or equivalent).

5.7 Detector - Electron Capture Detector.

6.0 REAGENTS

6.1 Reagent Water - Water in which an interferent is not

observed at the MDL of the parameter of interest.

6.2 Sodium Hydroxide Solution (10 N) - Dissolve 40 g of NaOH (ACS) in reagent water and dilute to 100 ml.

6.3 Sodium Thiosulfate - (ACS) Grannular.

6.4 Sulfuric Acid (1+1) - Slowly, add 50 ml of conc. H_2SO_4 (ACS, sp. gr. 1.84) to 50 ml of reagent water.

6.5 Acetone, hexane, isooctane, methylene chloride - pesticide quality.

6.6 Ethyl Ether - Nanograde, redistilled in glass if necessary. Ethyl ether must be shown to be free of peroxide before it is used.

6.7 Sodium Sulfate - (ACS) Grannular, Anhydrous. Purify by heating at 400^0C for 4 hours in a shallow tray.

6.8 Alumina - neutral, super I woelm or equivalent. Prepare activity III by adding 7% (V/W) reagent water to the Super I neutral alumina. Tumble or shake in a wrist action shaker for a minimum od 2 hours or preferably overnight. There shall be no lumps present. Store in a tightly sealed glass container. A 25 cycle soxhlet extraction of the alumina with methylene chloride is required if a solvent blank analyzed by the pesticide technique indicate any interferences for the compounds of interest.

6.8.1 Alumina Equivalency Check. Test the alumina by adding the BNA surrogate in 1:1 acetone/hexane to the alumina and follow the procedure in Section 7.0. The tribromophenol shall not be detected by GC/EC if the alumina and its activation are acceptable. Also check recovery of all single pesticides following the sample procedure. The percent recovery for all single pesticide must be greater than 80%, except for endosulfan sulfate which must be equal to or greater than 60% and endrin aldehyde which is not recovered.

6.9 Mercury - Triple distilled.

6.10 Copper powder - Activated.

6.11 Stock Standard solutions (1.00 ug/ul) - Stock standard solution can be prepared from pure standard materials or purchased as certified solutions.

6.12 Pesticide surrogate standard spiking solution -

6.12.1 The surrogate standrad is added to all samples and calibration standard solutions; the compound specified for this purpose is dibutylchlorendate.

6.12.2 Prepare a surrogate stndard spiking solution at a concentraion of 0.2 ug/1.00 mL acetone. Store the spiking solutions at 4^0C ($\pm 2^0$C) in Teflon-sealed containers. The solutions shall be checked frequently for stability. These solutions must be replaced after 12 months, or sooner, if comparison with quality control check samples indicates a problem.

6.13 Pesticide Matrix standard spiking solution -

Prepare a spiking solution of acetone or methanol that contains the following pesticides in the concentration specified:

Pesticide	ug/1.0 mL
Lindane	0.04
Heptachlor	0.04
Aldrin	0.04
Dieldrin	0.10
Endrin	0.10
4,4'-DDT	0.10

Matrix spikes are also to serve as duplicates by spiking two 1-liter portions from the one sample chosen for spiking.

7.0 CALIBRATION

7.1 Establish gas chromatographic operating conditions equivqlent to those given in Table 2.The gas chromatographic system must be calibrated using the external standard technique.

7.2 External Standard Calibration Procedure:

7.2.1 Prepare calibration standards at a minimum of three concentration level for each parameter of interest by adding volumes of one or more stock standard solutions to a volumetric flask and diluting to volume with isooctane. One of the external standards should be at a concentration near, but above the MDL (Table 1), and the other concentrations should correspond to the expected range of concentrations found in real samples or shall define the working range of the detector.

7.2.2 Using injection of 2 to 5 ul, analyze each calibration standard according to Section 10.1 and tabulate peak height or peak ares responses against the mass injected. The results are used to prepare a calibraiton curve for each compound.

8.0 QUALITY ASSURANCE/QUALITY CONTROL REQUIREMENTS

8.1 Determination of Retention Time Window

Before performing any sample analysis, the laboratory shall determine the retention time window for each pesticides/PCB target compound listed in Table 1 and surrogate spike compound (Dibutylch;lorendate). The retention time windows are used to make tentative identification of pesticide/PCBs during the sample analysis.

8.1.1 Prior to eatablishing the retention time windows, the GC operating conditions (oven temperature and flow rate) shall be adjusted such that 4,4'-DDT has a retention time of >12 minutes on packed GC columns except on OV-1 or OV-101 columns.

8.1.2 The retention time windows shall be established as follows:

8.1.2.1 At the beginning of the project and each time a new GC column is installed, make three injections of all single component pesticides mixtures, multi-response pesticides, and PCBs throughout the course of 72-hour period. The concentration of each pesticides/PCB shall be sufficient to provide a response that is approximately half scale. The three injections of each compound shall be made at approximately equal intervals during 72-hour period (i.e., each compound shall be injected near the beginning,near the middle, and near the end of the 72 hour period).

8.1.2.2 Verify the retention time shift for dibutylchlorendate in each standard. The retention time shift between the initial and subsequent standards shall be less than 2.0% difference for packed columns, less than 1.5% for wide bore capillary columns (ID less than 0.32mm). If this criteria is not met, continue injecting replicate standards to meet this criteria.

8.1.2.3 Calculate the standard deviation of the three absolute retention times for each single component pesticide. For multi-response pesticides or PCBs, choose one major peak from the envelope and calculate the standard deviation of the three retention time for that peak.

8.1.3 The standard deviation calculated in 8.1.2.3 shall be used to determine the retention time windows for a particular 72-hour sequence. Apply plus or minus three times the standard deviations in 8.1.2.3 to the retention time of each pesticide/PCB for the first analysis of the pesticide/PCB standard in a given 72-hour analytical sequence. This range of retention times defines the retention time window for the compound of interest for that 72-hour sequence.

8.2 Analysis of Method Blank

8.2.1 A method blank is a volume of deionized, distilled laboratory water for water samples carried through the entire analytical scheme (extraction, concentration, and analysis). The volume of method blank must be approximately equal to the sample volumes being processed.

8.2.2 Method blank analysis shall be analyzed at the frequency of one per every 20 samples analyzed.

8.2.3 The method blank must contain less than or equal to the quantitation limits of any sample pesticide/PCB target compounds. If the laboratory method blank exceeds these criteria, the laboratory shall investigate and appropriate corrective measures must be taken and document before further sample analysis proceeds.

8.3 Surrogate Spike Recovery

All standards, samples, blanks, matrix spike and matrix spike duplicate samples will be spiked with the surrogate spike compound (Dibutylchlorendate); and the spike amount and the recovery of surrogate spike compound shall meet the following requirements:

8.3.1 The Surrogate spiking standard compound shall be spiked into the samples, blanks and patrix spike and matrix spike duplicates before extration at a concentration of 0.2 ug/L (or 0.2 ppb).

8.3.2 The surrogate standard recovery shall be in the

range of 24-154%.

8.4 Matrix Spike/Matrix Spike Duplicate Analysis

8.4.1 Matrix spike / matrix spike duplicates shall be prepared and analyzed at a frequency of one per group of 20 or fewer field samples.

8.4.2 The matrix spiking standard solution shall contain those compounds specified in Section 6.13 at a concentration of 0.1 and 0.2 ug/mL respectively.

8.4.3 The matrix spiking standard solution shall be added to sample aliquots prior to the extractions.

8.4.4 Sample requring optiomal dilution and choosen as the matrix spike/matrix spike duplicate samples must be analyzed at the same dilution as the original unspiked samples. Calculate the matrix spike recovery and the relative percent difference (RPD) as follows:

$$\text{Matrix spike Percent Recovery} = \frac{SSR - SR}{SA} \times 100$$

Where:

SSR = Spiked sample results.

SR = Sample results.

SA = Spiked added from Spike Mix.

$$\text{Relative Percent Difference (RPD)} = \frac{D_1 - D_2}{(D_1 + D_2)/2} \times 100$$

Where:

D_1 = First sample value.

D_2 = Second sample value (duplicate).

8.4.5 The matrix spike/matrix spike duplicates recovery shall fall within the following ranges:

Fraction	Matrix Spike Compound	%Recovery
Pesticide	Lindane	56-123
Pesticide	Heptachlor	40-131
Pesticide	Aldrin	40-120
Pesticide	Dieldrin	52-126
Pesticide	Endrin	56-121
Pesticid	4,4'-DDT	38-127

8.5 External Standard Quantitation method must be used to quantitate all pesticide/PCBs before performing any sample analysis, the laboratory shall determine the retention time window for each pesticide/PCB target compounds listed in Table 1.

9.0 SAMPLE PREPARATION

9.1 Sample Collection, Preservation, and Handling

9.1.1 Grab samples must be collected in glass containers.

9.1.2 All samples must be iced or refrigerated at 4°C. If samples will not be extracted within 72 hours of collection, the sample shall be adjusted to a pH of 5.0-9.0 with sodium hydroxide or sulfuric acid. If aldrin is to be determined, add sodium thiosulfate when residual chlorine is present.

9.1.3 All sample must be extracted within 5 days of collection and completely analyzed within 40 days of extraction.

9.2 Sample Extraction - Separatory Funnel

9.2.1 Using a 1-liter graduated cylinde, measure out a 1-liter sample aliquot and place it into a 2-liter separatory funnel. Check the pH of the sample with wide range pH paper and adjust to between pH 5 and 9 with 10N sodium hydroxide and/or 1:1 sulfuric acid solution. (NOTE: Recovery of dibutylchlorendate will be

low if pH is outside this range. Alpha-BHC, Gamma-BHC, Endosulfan I and II, and Endrin are subject to decomposition under alkaline conditions, and therefore may not be detected if the pH is above 9.) Pipet 1.0 ml of surrogate standard spiking solution into the separatory funnel and mix well. Add 1.0 ml of pesticide matrix spiking solution to each of two 1-liter portions from the sample selected for spiking.

9.2.2 Add 60 ml methylene chloride to the separatory funnel and extract the sample by shaking the funnel for two minutes, with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface between layers is more than one-third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optium technique depends upon the sample, and may include: stirring, filtration of the emulsion through glass wool, centrifugation, or other physical means. Drain methylene chloride into a 250 ml Erlenmeyer flask.

9.2.3 Add a second 60 ml volume of methylene chloride to the sample bottle and repeat the extraction procedure a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner.

9.2.4 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-ml concentrator tube to a 500-ml evaporator flask. Other concentration devices or techniques may be used in place of the K-D if equivalency is demonstrated for all pesticides.

9.2.5 Pour the combined extract through a drying column containing about 10 cm of anhydrous granular sodium sulfate, and collect the extract in the K-D concentrator. Rinse the Erlenmeyer flask and column with 20 to 30 ml of methylene chloride to complete the quantitative transfer.

9.2.6 Add one or two clean boiling chips to the evaporator flask and attach a three-ball snyder column. Pre-wet the snyder column by adding about 1 ml of methylene chloride to the top. Place the K-D apparatus on a hot water bath (80 to 90^{0}C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with the vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 10 to 15 minutes. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flooded with condensed solvent. When the apparent volume of liquid reaches 1 ml, remove the K-D apparatus. Allow it to drain and cool for at least 10 minutes.

9.2.7 Momentarily remove the Snyder column, add 50 ml of hexane and a new boiling chip and re-attach the Snyder column. Pre-wet the column by adding about 1 ml of hexane to the top. Concentrate the solvent extract as before. The elapsed time of concentration should be 5 to 10 minutes. When the apparent volume of liquid reaches 1 ml, remove the K-D apparatus and allow it to drain and cool at least 10 minutes.

9.2.8 Remove the Snyder column, rinse the flask and its lower joint into the concentrator tube with 1 to 2 ml of hexane. If sulfur crystal are a problem, proceed to paragraph 9.4.2; otherwise continue to paragraph 9.2.9.

9.2.9 Nitrogen Blowdown Technique

Place the concentrator tube in a warm water bath (35^{0}C) and evaporate the solvent volume to 0.5 ml using a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon). **CAUTION: New plastic tubing must not be used between the carbon trap and the sample, as it may introduce interference. The internal wall of the tube must be rinsed down several times with hexane during the operation and the final volume brought to 0.5 ml. During**

evaporation, the tube solvent level must be kept below the water level of the bath. The extract must be never be allowed to become dry.

9.2.10 Dilute the extract to 1 ml with acetone and proceed to Alumina Column Cleanup.

9.3 Sample Extraction - Continuous Liquid-Liquid Extractor

9.3.1 When experience with a sample from a given source indicate that a serious emulsion problem will result, or if an emulsion is encountered in 9.2.2 using a separatory funnel, a continuous extractor shall be used.

9.3.2 Using a 1-liter graduated cylinder, measure out a 1-liter sample aliquot and place it into the continuous extractor. Pipet 1.0 ml of surrogate standard spiking solution into the continuous extractor and mix well. Check the pH of the sample with wide range pH paper and adjust to between pH 5 and 9 with 10 N sodium hydroxide and/or 1:1 sulfuric acid solution.

9.3.3 Add 500 ml of methylene chloride to the distilling flask. Add sufficient reagent water to ensure proper operation and extract for 18 hours. Allow to cool, then detach the boiling flask and dry. Concentrate the extract as in 9.2.4 through 9.2.10 .

9.4 Cleanup and Separation

9.4.1 Alumina Column Cleanup

9.4.1.1 Add 3 g of activity III neutral alumina to the 10-ml chromatographic column. Tap the column to settle the alumina. Do not pre-wet the alumina.

9.4.1.2 Transfer the 1 ml of hexane/acetone extract from 9.2.10 to the top of the alumina using a disposable Pasteur pipet. Collect the eluate in a clean 10-ml concentrator tube.

9.4.1.3 Add 1 ml of hexane to the original extract concentrator tube to rinse it. Transfer these rinsings to the alumina column. Elute the column with an additional 9 ml of hexane. Do not allow the column to go dry during the addition and elution of the sample.

9.4.1.4 Adjust the extract to a final volume of 1 ml using hexane.

9.4.1.5 The pesticide/PCB fractionis ready for analysis. Proceed to Section 10.0. Store the extract at 4^0C ($+2^0C$) in the dark in Teflon sealed containers until analyses are performed.

9.4.2 Optional Sulfur Cleanup

9.4.2.1 Concentrate the hexane extract from Section 9.2.8 to 1 ml.

9.4.2.2 Transfer the 1 ml to a 50 ml clear glass bottle or vial with a Teflon-lined screw cap. Rinse the concentrator tube with 1 ml of hexane, adding the rinsings to the 50 ml bottle.

9.4.2.3 Add 1 ml TBA-sulfite reagent and 2 ml of 2-propanol,cap the bottle, and shake for at least 1 minutes. If the sample is colorless or if the initial color is unchanged, and if clear crystal (precipitated sodium sulfite) are observed, sufficient sodium sulfite is present. If the precipitated sodium sulfite disappears, add more crystalline sodium sulfite in approximately 100 mg portions until a solid residue remains after repested shaking.

9.4.2.4 Add 5 ml of distilled water and shake for at least 1 minute. Allow the sample to stand 5-10 minutes. Transfer the hexane layer (top) to a concentrator ampul and go back to Section 9.2.9 .

10.0 SAMPLE ANALYSIS

10.1 PRIMARY ANALYSIS (PRIMARY GC COLUMN, GC/EC)

Samples are analyzed according to the sequence described in Figure 1. Quantitation may be performed on primary or confirmation analysis.

Adjust oven temperature and carrier gas flow rates so that the retention time for 4,4'-DDT is equal to or greater than 12 minutes. The operating conditions for the gas chromatographic separation shall produce peak resolutions of 25% or greater. The percent resolution is calculated by dividing the height of the valley by the peak height of the smaller peak being resolved, multiplied by 100. This criteria shall be considered when determining whether to quantitate on the primary column analysis of the confirmation (secondardy column) analysis. When this criteri can not be met, quantiation is adversely affected because of the difficulty in determining where to establish the baseline.

Inject 2 to 5 ul of the sample or standard extracts using the solvent-flush technique or auto sampler. Record the volume injected to the nearest 0.05 ul and the total extract volume. **NOTE: Dibutylchlorendate recovery may bbe calculated from a capillary or packed column GC/EC meeting all QC requirements for quantitation. However, matrix spike duplicates must be quantitated on a packed column.**

10.1.1 Inject Individual Standard Mix A and B and all multi-response pesticides/PCBs at the beginning of each 72 hours sequence. To establish the RT window within each 72 hours sequence for the pesticides/PCB of interest, use the absolute RT from the above chromatograms as the mid-point, and + three times the standard deviation calculated for each compound. Individual Standard A and B are analyzed alternately, and intermittenly throughout the analysis as in Figure 1. Any pesticide outside of its established retention time window requires immediate investigation and correction before continuing the analysis. The laboratory must reanalyze all affected samples.

FIGURE 1

THE 72 HOURS SEQUENCE FOR PESTICIDE/PCB ANALYSIS

1. Evaluation Standard Mix A
2. Evaluation Standard Mix B
3. Evaluation Standard Mix C
4. Individual Standard Mix A*
5. Individual Standard Mix B*
6. Toxaphene
7. Aroclors 1016/1260
8. Aroclor 1221**
9. Aroclor 1232**
10. Aroclor 1242
11. Aroclor 1248
12. Aroclor 1254
13. 5 Samples
14. Evaluation Standard Mix B
15. 5 Samples
16. Evaluation Standard Mix A or B
17. 5 Samples
18. Evaluation Standard Mix B
19. 5 Samples
20. Individual Standard Mix A or B (Whichever not run in step 16)
21. 5 Samples
22. Repeat the Above sequence starting with Evaluation Standard B (Step 14 above
23. Pesticide/PCB analysis sequence must end with individual Standard Mix A and B regardless of number of samples analyzed.

* These may be combined into one mixture.

** Aroclor 1221 and 1232 must be analyzed one each instrument and each cloumn at a minimum of once per month. Copies of these chromatograms must be submitted for sample analyses performed during the applicable month.

10.1.2 Sample analysis of extracts from Section 9.0 (Sample preparation) can begin **ONLY** when linearity and degradation QA/QC requirements specified in Section 8.0 have been met.

NOTE: The 10% RSD linearity criteria is only required on the column(s) being used for pesticides/PCBs quantitation. If a column is used for surrogate quantitation only, the 10% RSD is required only for dibutylchlorendate.

Analyze samples in groups of no more than 5 samples. After the analysis of the first group of up to 5 samples, analyze Evaluation Standard Mix B. Analyze another group of up to 5 samples, followed by the analysis of Individual Mix A or B. Subsequent groups of up to 5 samples may be analyzed by repeating this sequence. Alternately analyzing Evaluation Standard Mix B and Individual Mix A or B between the groups as shown in Figure 1. The pesticide/PCB analytical sequence must end with individual Mix A and B regardless of the number of samples analyzed (Figure 1).

If a multiresponse pesticide/PCB is detected in either of the preceeding groups of 5 samples, the appropriate multiresponse pesticide/PCB may be substituted for Individual Mix A or B.

If the samples are split between 2 or more instruments, the complete set of standards must be analyzed on each instrument with the same 72-hour requirements. All standard must analyzed prior to the samples to avoid the effects of poor chromatography caused by the unsuspected injection of a highly concentrated sample.

10.1.3 If one or more of the criteria have been violated during the 72-hour sequence, stop the run and take corrective action. After corrective action has been taken, the 72-hour sequence may be restarted as follows:

10.1.3.1 If a standard violated the criteria,

restart the sequence with that standard, determine that the criteria have been met, and continue with sample analyses according to Figure 1.

10.1.3.2 If a sample violated the criteria, restart the sequence with the standard that would have followed that group of samples, determine that the criteria have been met, and continue with sample analyses according to Figure 1.

10.1.4 If it is determined after the 72-hour sequence that one or more of the criteria have been violated, proceed as follows:

10.1.4.1 If a standard violated the criteria, all samples analyzed after that standard must be reanalyzed a spart of a new 72-hour sequence.

10.1.4.2 If a subsequent standard in the original sequence met all the criteria, then only those samples analyzed between the standard that did not meet the criteria and the standard that did meet the criteria must be reanalyzed as part of a new 72-hour sequence.

10.1.4.3 If only samples violated the criteria, then those samples must be reanalyzed as part of a new sequence.

10.1.5 Sample must also be repested if the degradation of DDT and/or endrin exceeds 20.0% respectively on the intermittent analysis of Evaluation Standard Mix B.

10.2 CONFIRMATION ANALYSIS (SECONDARY COLUMN, GC/EC)

10.2.1 Confirmation analysis is to confirm the presence of compounds tentatively identified in the primary analysis (10.1). Therefore the only standards that are required are the Evaluation Standard Mixes (to check linearity

and degradation criteria) and standards of all compounds to be confirmed. The 72 hours sequence shown in Figure 1 is therefore modified to fit such case. Quantitation may be performed on the cinfirmation analysis. **NOTE: If toxaphene or DDT is to be quantitated, additional linearity requirements are specified in 10.1.2**

10.2.2 The peak resolution criteria of 25% or greater between peaks shall be observed when determining whether tc quantitate on the confirmation analysis (See 10.1). If a fused silica capillary column (FSCC) is used, the peak resolution criteria shall be checked for the following pesticide pairs: a) Beta-BHC and Delta-BHC; b) Dieldrin and 4,4'-DDT; c) 4,4'-DDD and Endrin Aldehyde; d) Endosulfan sulfate and 4,4'-DDT.

10.2.3 All QC requirements specified for primary GC column analyiss shall be observed.

10.2.4 Begin the confirmation analysis GC sequence with the three concentration levels of Evaluation Standard Mixes A, B, and C. The exception to this occurs when toxaphene and/or DDT series are to be confirmed and quantitated. There are four combinations of pesticides that could occur, therefore the following sequence must be followed depending on the situation:

10.2.4.1 Toxaphene Only -

Begin the sequence with Evaluation Standard Mix B to check degradation, followed by three concentration levels of toxaphene. Check linearity by calculating the %RSD.If %RSD <10.0%, then use the Equation 1 for calculation. If %RSD > 10.0%, then plot a standard curve and determine the nanogram for each sample in that set from the curve.

10.2.4.2 DDT, DDE, DDD Only -

Begin the sequence with Evaluation Standard Mix B. Then inject three

concentration levels of a standard containing DDE, DDD, and DDT. Calculate linearity and follow the requirements specified in 10.2.4.1. for each compound to be quantitated.

10.2.4.3 DDT Series and Toxaphene -

Begin the sequence with Evaluation Standard Mix B. Then inject three concentration levels of toxaphene and another three levels of the DDT series. Calculate linearity and follow the requirements specified in 10.2.4.1 for each compound to be quantitated.

10.2.4.4 Other Pesticides/PCBs Plus DDT Series and/Or Toxaphene

Begin the sequence with Evaluation Standard Mixes A, B, and C. Calculate linearity of the four compounds in the Evaluation Standard Mixes. If DDT and/or one or more of the other compounds have RSD > 10.0% and/or degradation exceed the criteria, corrective action shall be performed before repesting the above chromatography evaluation.

If only DDT exceed the linearity and one or more of the DDT series is to be quantitated, follow the procedure for DDT,DDE, and DDD only in 10.2.4.2.

If none of the DDT series is to be quantitated and DDT exceed the 10%RSD criteria, simply report the %RSD on the proper form. Anytime toxaphene is to be quantitated, procedure in 10.2.4.1 shall be used.

10.2.5 After the linearity sstandards required in 10.2.4 are injected, continue the confirmation analysis injection sequence with all compounds tentatively identified during the primary GC column analysis to establish the daily retention time windows during primary analysis. Analyze

and the validation and signature by the laboratory manager.

12.2.2 Sample Data

Sample data shall be reported using the Organic Analysis Data Reporting Forms (Attachment I) for all samples, arranging in increasing alphanumeric sample number order, followed by the QC analysis data, quarterly verification of instrument parameter forms, raw dataincluding copies of the sample custody records and sample preparation logs.

12.2.2.1 FORM I (Pesticides Organic Analysis Data Sheet)

12.2.2.2 FORM II (Pesticides Surrogate Recovery)

12.2.2.3 FORM III (Pesticides Matrix Spike/Matrix Spike Duplicate (MS/MSD) Recovery)

12.2.2.4 FORM IV (Pesticides Method Blank)

12.2.2.5 FORM VIII A (Pesticides Evaluation Standard Summary)

12.2.2.6 FORM VIII B (Evaluation of Retention Time Shift for Dibutylchlorendate)

12.2.2.7 FORM IX (Pesticides/PCBs Standard Summary)

12.2.2.8 FORM X (Pesticides/PCBs Identification)

12.2.2.10 RAW DATA

Raw data shall include all instrument printouts used for the sample results, including those readout that fall below

the method detection limits, and copies of GC chromatograms. Raw data must be labelled with project name, field sample number, time and date of each analysis, instrument used.

13.0 REFERENCES

13.1 "Determination of pesticides and PCBs in industrial, and municipal Wastewaters." EPA-600/4-82-023, U.S.Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, 45268,June, 1982.

13.2 40 CFR Part136, Appendix B.

PESTICIDE ORGANICS ANALYSIS DATA SHEET

Lab Name:_____

Field Sample Number_____.

Matrix: water

Lab Sample ID: _____

Sample vol: _____ mL

Lab File ID: _____

Level: (low/med) _____

Date Received: _____

Date Extracted:_____

Extraction: (SepF/Cont/Sonc) _____

Date Analyzed: _____

GPC Cleanup: (Y/N)___ pH:___

Dilution Factor: _____

CAS NO.	COMPOUND	CONCENTRATION UNITS: (ug/L	Q
319-84-6	alpha-BHC		
319-85-7	beta-BHC		
319-86-8	delta-BHC		
58-89-9	gamma-BHC (Lindane)		
76-44-8	Heptachlor		
309-00-2	Aldrin		
1024-57-3	Heptachlor epoxide		
959-98-8	Endosulfan I		
60-57-1	Dieldrin		
72-55-9	4,4'-DDE		
72-20-8	Endrin		
33213-65-9	Endosulfan II		
72-54-8	4,4'-DDD		
1031-07-8	Endosulfan sulfate		
50-29-3	4,4'-DDT		
72-43-5	Methoxychlor		
53494-70-5	Endrin ketone		
5103-71-9	alpha-Chlordane		
5103-74-2	gamma-Chlordane		
8001-35-2	Toxaphene		
12674-11-2	Aroclor-1016		
11104-28-2	Aroclor-1221		
11141-16-5	Aroclor-1232		
53469-21-9	Aroclor-1242		
12672-29-6	Aroclor-1248		
11097-69-1	Aroclor-1254		
11096-82-5	Aroclor-1260		

WATER PESTICIDE SURROGATE RECOVERY

Lab Name: _____

	Field SAMPLE NO.	S1 (DBC) #	OTHER
01			
02			
03			
04			
05			
06			
07			
08			
09			
10			
11			
12			
13			
14			
15			
16			
17			
18			
19			
20			
21			
22			
23			
24			
25			
26			
27			
28			
29			
30			

ADVISORY QC LIMITS

S1 (DBC) = Dibutylchlorendate (24-154)

Column used to flag recovery values

* Values outside of QC limits

D Surrogates diluted out

WATER PESTICIDE MATRIX SPIKE/[illegible] DUPLICATE RECOVERY

Lab Name:_____

Lab Sample I.D. _____. Field Sample number_____.

Matrix Spike - EPA Sample No.: _____

COMPOUND	SPIKE ADDED (ug/L)	SAMPLE CONCENTRATION (ug/L)	MS CONCENTRATION (ug/L)	MS % REC #	QC LIMITS REC.
gamma-BHC (Lindane)____	_____	_____	_____	_____	56-123
Heptachlor_____	_____	_____	_____	_____	40-131
Aldrin_____	_____	_____	_____	_____	40-120
Dieldrin_____	_____	_____	_____	_____	52-126
Endrin_____	_____	_____	_____	_____	56-121
4,4'-DDT_____	_____	_____	_____	_____	38-127
_____	_____	_____	_____	_____	_____

COMPOUND	SPIKE ADDED (ug/L)	MSD CONCENTRATION (ug/L)	MSD % REC #	% RPD #	QC LIMITS RPD	QC LIMITS REC.
gamma-BHC (Lindane)____	_____	_____	_____	_____	15	56-123
Heptachlor_____	_____	_____	_____	_____	20	40-131
Aldrin_____	_____	_____	_____	_____	22	40-120
Dieldrin_____	_____	_____	_____	_____	18	52-126
Endrin_____	_____	_____	_____	_____	21	56-121
4,4'-DDT_____	_____	_____	_____	_____	27	38-127
_____	_____	_____	_____	_____	_____	_____

Column to be used to flag recovery and RPD values with an asterisk

* Values outside of QC limits

RPD:_____ out of _____ outside limits
Spike Recovery:_____ out of _____ outside limits

COMMENTS: _____

_____

PESTICIDE METHOD BLANK SUMMARY

Lab Name: _____

Lab Sample ID: _____ Lab File ID: _____

Matrix: water Level: (low/med) _____

Date Extracted: _____ Extraction: (SepF/Cont/Sonc) _____

Date Analyzed (1): _____ Date Analyzed (2): _____

Time Analyzed (1): _____ Time Analyzed (2): _____

Instrument ID (1): _____ Instrument ID (2): _____

GC Column ID (1): _____ GC Column ID (2): _____

THIS METHOD BLANK APPLIES TO THE FOLLOWING SAMPLES, MS AND MSD:

	Field SAMPLE NO.	LAB SAMPLE ID	DATE ANALYZED 1	DATE ANALYZED 2
01				
02				
03				
04				
05				
06				
07				
08				
09				
10				
11				
12				
13				
14				
15				
16				
17				
18				
19				
20				
21				
22				
23				
24				
25				
26				

COMMENTS: _____

_____

PESTICIDE EVALUATION STANDARDS SUMMARY

Lab Name:_____

Instrument ID:_____ GC Column ID: _____

Dates of Analyses:_____ to _____

Evaluation Check for Linearity

PESTICIDE	CALIBRATION FACTOR EVAL MIX A	CALIBRATION FACTOR EVAL MIX B	CALIBRATION FACTOR EVAL MIX C	%RSD (</= 10.0%)	
Aldrin					
Endrin					
4,4'-DDT					(1)
DBC					

(1) If > 10.0% RSD, plot a standard curve and determine the ng for each sample in that set from the curve.

Evaluation Check for 4,4'-DDT/Endrin Breakdown (percent breakdown expressed as total degradation)

		DATE ANALYZED	TIME ANALYZED	ENDRIN	4,4'-DDT	COMBINED (2)
	INITIAL EVAL MIX B					
01	EVAL MIX B					
02	EVAL MIX B					
03	EVAL MIX B					
04	EVAL MIX B					
05	EVAL MIX B					
06	EVAL MIX B					
07	EVAL MIX B					
08	EVAL MIX B					
09	EVAL MIX B					
10	EVAL MIX B					
11	EVAL MIX B					
12	EVAL MIX B					
13	EVAL MIX B					
14	EVAL MIX B					

(2) See Form instructions.

PESTICIDE EVALUATION STANDARDS SUMMARY
Evaluation of Retention Time Shift for Dibutylchlorendate

Lab Name:_____

Instrument ID:_____ GC Column ID: _____

Dates of Analyses:_____ to _____

	Field SAMPLE NO.	LAB SAMPLE ID	DATE ANALYZED	TIME ANALYZED	% D	*
01						
02						
03						
04						
05						
06						
07						
08						
09						
10						
11						
12						
13						
14						
15						
16						
17						
18						
19						
20						
21						
22						
23						
24						
25						
26						
27						
28						
29						
30						
31						
32						
33						
34						
35						
36						
37						
38						

* Values outside of QC limits (2.0% for packed columns, 0.3% for capillary columns)

PESTICIDE/PCB STANDARDS SUMMARY

Lab Name:_____

Instrument ID:_____ GC Column ID: _____

	DATE(S) OF ANALYSIS FROM: TO:			DATE OF ANALYSIS:			
	TIME(S) OF ANALYSIS FROM: TO:			TIME OF ANALYSIS:			
				EPA SAMPLE NO. (STANDARD)			
COMPOUND	RT	RT WINDOW FROM	RT WINDOW TO	CALIBRATION FACTOR	RT	CALIBRATION FACTOR	QNT Y/N	%D
alpha-BHC								
beta-BHC								
delta-BHC								
gamma-BHC								
Heptachlor								
Aldrin								
Hept. epoxide								
Endosulfan I								
Dieldrin								
4,4'-DDE								
Endrin								
Endosulfan II								
4,4'-DDD								
Endo. sulfate								
4,4'-DDT								
Methoxychlor								
Endrin ketone								
a. Chlordane								
g. Chlordane								
Toxaphene								
Aroclor-1016								
Aroclor-1221								
Aroclor-1232								
Aroclor-1242								
Aroclor-1248								
Aroclor-1254								
Aroclor-1260								

Under QNT Y/N: enter Y if quantitation was performed, N if not performed. %D must be less than or equal to 15.0% for quantitation, and less than or equal to 20.0% for confirmation.

Note: Determining that no compounds were found above the CRQL is a form of quantitation, and therefore at least one column must meet the 15.0% criteria.

For multicomponent analytes, the single largest peak that is characteristic of the component should be used to establish retention time and %D. Identification of such analytes is based primarily on pattern recognition.

PESTICIDE/PCB IDENTIFICATION

Lab Name:_____

GC Column ID (1): _____ GC Column ID (2): _____

Instrument ID (1): _____ Instrument ID (2): _____

Lab Sample ID: _____

Lab File ID: _____ (only if confirmed by GC/MS)

PESTICIDE/PCB	RETENTION TIME		RT WINDOW OF STANDARD FROM	TO	QUANT? (Y/N)	GC/MS? (Y/N)
01_____	Column 1	_____	_____	_____	-	-
02	Column 2	_____	_____	_____	-	-
03_____	Column 1	_____	_____	_____	-	-
04	Column 2	_____	_____	_____	-	-
05_____	Column 1	_____	_____	_____	-	-
06	Column 2	_____	_____	_____	-	-
07_____	Column 1	_____	_____	_____	-	-
08	Column 2	_____	_____	_____	-	-
09_____	Column 1	_____	_____	_____	-	-
10	Column 2	_____	_____	_____	-	-
11_____	Column 1	_____	_____	_____	-	-
12	Column 2	_____	_____	_____	-	-

Comments: _____

Appendix C

Warzyn Inc.
Low-Level Detection Methods for Water Supply Sample Analysis

Metals
Cyanide

Metals

INORGANIC TARGET ANALYTE LIST AND REQUIRED INSTRUMENT DETECTION LIMITS FOR WATER SUPPLY WELLS

Compound	Required Instrument Detection Limit (ug/L)[1]		
	GFAA	ICP	Other
Aluminum		100	
Antimony [2]	5		
Arsenic	5		
Barium		50	
Beryllium		5	
Cadmium [2]	0.5		
Calcium		1000	
Chromium		10	
Cobalt		10	
Copper		10	
Iron		100	
Lead [2]	3		
Magnesium		1000	
Manganese		10	
Mercury			0.2
Nickel		20	
Potassium			2000
Selenium	2		
Silver [2]	5		
Sodium			1000
Thallium	3		
Vanadium [2]	10		
Zinc		20	
Cyanide			10

1 Instrument Detection Limits (IDL) must be met before any samples are analyzed. The lab may submit their quarterly Form XI with each case if all IDLs meet the detection limit requirements. If detection limits cannot be met by using ICP, the use of GFAA is required.

2 ICP analysis results can only be reported for antimony, cadmium, lead, silver and vanadium if the concentration is $\geq$ 10 times the IDL of the instrument used. If ICP results are reported, all ICP audits are required including matrix spike.

Effective Date: 3-14-90

ATOMIC ABSORPTION SPECTROMETRY

Furnace - Direct Injection

Scope and Application: Metals in solution can be readily analyzed by Atomic Absorption Spectrometry using either flame, furnace or hydride techniques. The furnace - direct injection technique allows for lower detection limits. The use of the graphite platform in furnace analyzed can improve sensitivity and reduce some matrix interferences.

Method: Furnace; direct injection

Reference: EPA 1984, Section 200

- Analytical Methods for Zeeman Graphite Tube Atomizers - Varian 1986

- Spectra AA - 300/400 Zeeman Operation Manual - Varian March 1988

Sample Handling: Acidify with concentrated nitric acid to ph< 2. Drinking waters and filtered groundwater samples free of particulate matters and organics may be analyzed directly, while wastewaters, leachates, solids, etc., must be digested prior to analysis (refer to appropriate digestion procedures). Samples must be analyzed within 6 months.

Reagents and Apparatus:

1. Zeeman Automatic Absorption Spectrometer - 400
2. Zeeman Graphite tube Atomizer
3. IBM Personal System/2 Model 30 Computer
4. EPSON EX-800 Printer
5. Required metal lamp and power source
6. Stock and standard solutions for required metal
7. Class A volumetric glassware
8. Instr-analyzed nitric acid
9. Deionized water
10. Argon gas - prepurified
11. Graphite partition tubes
12. Graphite plateau tubes and platforms
13. Eppendorf 100-1000 microliter pipetor
14. Disposable 10 ml beakers

Procedure:

A. Power Up Procedure

1. Turn on argon gas and cooling water.

2. Always turn the system on in the following order: spectrometer, furnace, printer, and computer.

3. After the DOS prompt has been displayed, type "Zeeman" and press Enter. After a brief pause, an introductory message will then be displayed followed by the PROGRAM MODES page. You may now proceed to operate the system.

B. Automatic Run Using the Sampler

Notes:

a. Only programs which have been stored can be used for an automatic run.

b. For all programs, the method of sample introduction (INSTRUMENT PARAMETERS page) must be specified as SAMPLER AUTOMIXING or SAMPLER PREMIXED.

c. You may print your analytical results during the run or after the run (REPORT FORMAT).

d. If an automatic run is stopped and then restarted, the sampler will automatically perform a tube clean and run a blank. It will then continue on as per the instructions set in the SEQUENCE CONTROL page.

F9 through F12 are hard keys with their function on the supplied overlay. F1 through F6 are soft keys; their functions will change from one page to the next. The function for each soft key is displayed at the bottom of the screen and only those displayed are active for that page.

1. From the PROGRAM MODES page, press AUTOMATIC RUN. (The system will automatically display the SEQUENCE SELECTION page).

2. On the SEQUENCE SELECTION page, press F1 to Clear Sequence of previous element run. Then enter the numbers of the programs to be run. If more than one program is to be run, press ENTER after each element program number.

3. Return to the index and select p. 4 (INSTRUMENT PARAMETERS):

   Lamp position:
   Lamp current:
   Slit Width:
   Slit Height:
   Wave Length
   Sample Introduction:
   Measurement Time:
   Replicates:
   Background Correction:
   Max. Absorbance:

   The machine will automatically select the basic operating conditions set in the method for the element that you are selecting. Parameters may be changed by pressing the HOME key.

4. Return to the Index and select page 6 (OPTIMIZATION)

   a. Open the lamp turret cover and ensure that the required lamp is in the operating position.

   b. Observe the signal bar labelled ALIGN HC LAMP displayed on the video screen. Turn the horizontal lamp base adjusting screw (the top one of the two) fully clockwise. Now turn this screw slowly anti-clockwise until the first peak is detected (the length of the signal bar will increase). Continue adjusting this screw until the length of the signal bar is the maximum obtainable (if the signal bar is fully extended, press the RESCALE soft key [F1] to bring the signal bar back on scale and again adjust the screw to obtain maximum signal. Note particularly that turning the horizontal adjusting screw further anti-clockwise will produce a second peak. DO NOT align the lamp on this second peak - ALWAYS align the lamp on the first peak. Carefully adjust the vertical adjusting screw (the bottom one of the two) so that the length of the signal bar is the maximum obtainable (if necessary, use the RESCALE soft key to keep the signal bar on scale.)

   c. Record the photomultiplier voltage in the instrument log book. A constantly increasing voltage over time is evidence of decreasing efficiency of the element lamp. Monitor this voltage to determine when element lamps should be replaced.

   d. When switching from partition to platform tubes, you need to check the position of the graphite tube automizer:

      Hold a piece of white care between the righthand end of the graphite tube automizer and the sample compartment window. Use the furnace vertical adjust and position the automizer until light from the hollow certhode lamp is obviously passing through the graphite tube on to the card.

Remove the card. Observe the signal bar labelled ALIGN HC LAMP displayed on the video screen. Use the furnace vertical adjust and carefully adjust the position of the graphite tube automizer until the length of the signal bar is the maximum obtainable.

5. Perform daily maintenance. Check the condition of the graphite tube and replace as necessary.

6. Go the the next page: STANDARDS PAGE.

   a. This page tells which standards to use for calibration.

7. Go the next page: SAMPLER PAGE.

   a. This page lists the volume of standards, blanks, samples and modifier that will be used.

   b. Press F2 to align the sampler arm. Place a finger on the arm as it starts to descend into the furnace and gently lower the arm by hand. Carefully adjust the sampler position using the two adjustment knobs on the base of the autosampler so that the capillary is exactly in the center of the sample injection hole. With the capillary down in the furnace and using the mirror, turn the height adjusting screw so the capillary is about 1 mm above the bottom of the tube or platform.

8. Return to INDEX, type 13 and press F6 to call up REPORT FORMAT.

   a. Enter:

      - Operator Initials:
      - Date:
      - Batch Name:

   Use HOME key to select appropriate conditions for remaining parameters.

   If sample labels are to be printed, press F6 and enter appropriate labels.

9. Press F10 for Instrument Zero before the start of a run.

10. Press F11 to start Automatic Run.

FURNACE MAINTENANCE

The following maintenance is to be done each day the furnace is operated.

1. Clean the furnace windows.
   a. twist out furnace windows from furnace unit.
   b. Wipe windows with Q-tip soaked with alcohol.
   c. Rinse with DI water and dry with Kim-wipe
   d. Re-insert windows in furnace.
2. Check machine windows and clean if needed.
3. Wipe inside of furnace with Q-tip soaked in alcohol.
4. Fill the rinse bottle with DI water.
5. Open the syringe compartment door and pull the syringe assembly carefully out of its mounting. Remove the plunger from the syringe, and on SAMPLER page, press F3 to rinse the syringe and bleed any air bubbles from the syringe. Press F3 and rinse again, while water is dripping from syringe insert the plunger into the syringe. Wipe the syringe dry and re-insert.
6. Inserting Graphite Tube
   a. Swing toggle level on top of furnace fully clockwise to open furnace.
   b. Place graphite tube in the graphite shroud in the center block. Align sample introduction part of the graphite tube with the opening in the furnace block.
   c. Swing the toggle lever fully counter-clockwise and the righthand electrode assembly will automatically close on the center block.
   d. Before using a new graphite tube for analyses, use the tube clean utility (SIGNAL GRAPHICS page) 3-4 times to remove any contamination.

Effective Date 4-19-90

ANTIMONY - VARIAN 400

Method: AA - Furnace; Direct Injection

Reference: EPA 1984, Method 204.2

"Analytical Methods for Zeeman Graphite Tube Atomizers", Varian, 1986

Contact Laboratory Program, "Statement of Work"

Detection Limit: 0.005 mg/L

Optimum Concentration Range: 0.005 - 0.100 mg/L

Instrument Conditions:

Instrument Mode:	Absorbance
Calibration Mode:	Concentration
Measurement Mode:	Peak Area
Lamp Current (mA):	14
Slit Width (nm):	0.2
Slit Height:	Normal
Wavelength (nm):	217.6
Sample Introduction:	Sampler Premixed
Time Constant:	0.05
Measurement Time (sec):	2.0
Replicates:	2
Background Correction:	On
Maximum Absorbance:	1.40

FURNACE PARAMETERS

Step	Temp (*C)	Time (sec)	Gas Flow (L/min)	Gas Type	Read Command
1	85	5.0	3.0	NORMAL	NO
2	95	25.0	3.0	NORMAL	NO
3	120	10.0	3.0	NORMAL	NO
4	120	5.0	3.0	NORMAL	NO
5	900	10.0	3.0	NORMAL	NO
6	900	5.0	3.0	NORMAL	NO
7	900	2.0	0.0	NORMAL	NO
8	2300	1.0	0.0	NORMAL	YES
9	2300	2.0	0.0	NORMAL	YES
10	2300	2.0	3.0	NORMAL	NO

Sample Volume: 20 uL

Matrix Modifier Volume: 5 uL (0.25% Nickel Nitrate).

Standards to use for curve set-up: 25.0, 50.0, 100.0 ug/L.

Graphite Tube Type: Pyrolitic coated partition tube.

Sample Handling: Acidify with nitric acid to pH <2. Analyze within 6 months.

Reagent Preparation:

1. Standard Antimony Solution (1000 ug/L Antimony): Pipet 1.00 mL of the 1000 ppm stock antimony solution into a 1000 mL volumetric flask, add 1/2 mL HNO_3 and dilute to the mark with D.I. water. Prepare fresh daily.

2. Calibration standards: (Prepare fresh daily.)

Concentration of Standard	Volume of Antimony Standard	Dilute to
25.0 ug/L	2.5 mL of 1000 ug/L Sb	100 mL
50.0 ug/L	5.0 mL of 1000 ug/L Sb	100 mL
100 ug/L	10 mL of 1000 ug/L Sb	100 mL

3. Nickel Nitrate 0.25% Solution: In a 100 mL volumetric flask dissolve 1.25g of $Ni(NO_3)_2 \cdot 6H_2O$ in D.I. water and dilute to 100 mL. Prepare fresh every 6 months.

Notes:

1. Samples must be diluted to obtain concentrations within the optimum concentration range.

2. Standards are to be prepared in the same acid concentrations as the samples being analyzed.

3. The use of background correction is required.

4. The use of halide acids should be avoided.

5. Nickel nitrate is added as a matrix modifier to control interferences.

Procedure: For the analysis procedure, refer to the Atomic Absorption Spectrometry, Furnace - Direct Injection section of this manual.

If antimony is to be analyzed in the concentration mode, calibrate using the 25.0, 50.0, and 100 ug/l standards and follow the procedure for analysis in the concentration mode.

[METCONT]

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The absorbances should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, furnace alignment, lamp alignment, graphite tube, etc.).

2. A quality control calibration standard and a blank are to be analyzed, initially and after every 10 samples. If less than 10 samples are analyzed, a calibration standard and blank are still required. The last samples analyzed in the run are to be the calibration standard and blank. These standards must be within the acceptable ranges or the samples run after the last acceptable check standard are to be reanalyzed.

3. Analyze a standard at, or less than, the contract required detection limit after the initial calibration verification and blank.

4. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Spike recoveries and duplicate results are to be within acceptable ranges, or data must be flagged appropriately.

5. For every sample analyzed, an analytical spike (at the bench) must be run to verify that standard additions are not required. Criteria for standard additions is:

   a. If the spike recovery is within 85 - 115%, standard additions are not required.

   b. If the spike recovery is outside 85 - 115%, standard additions are required. (See the Furnace Decision Tree for more detail.)

6. An EPA reference standard will be analyzed with each analysis.

Calculations:

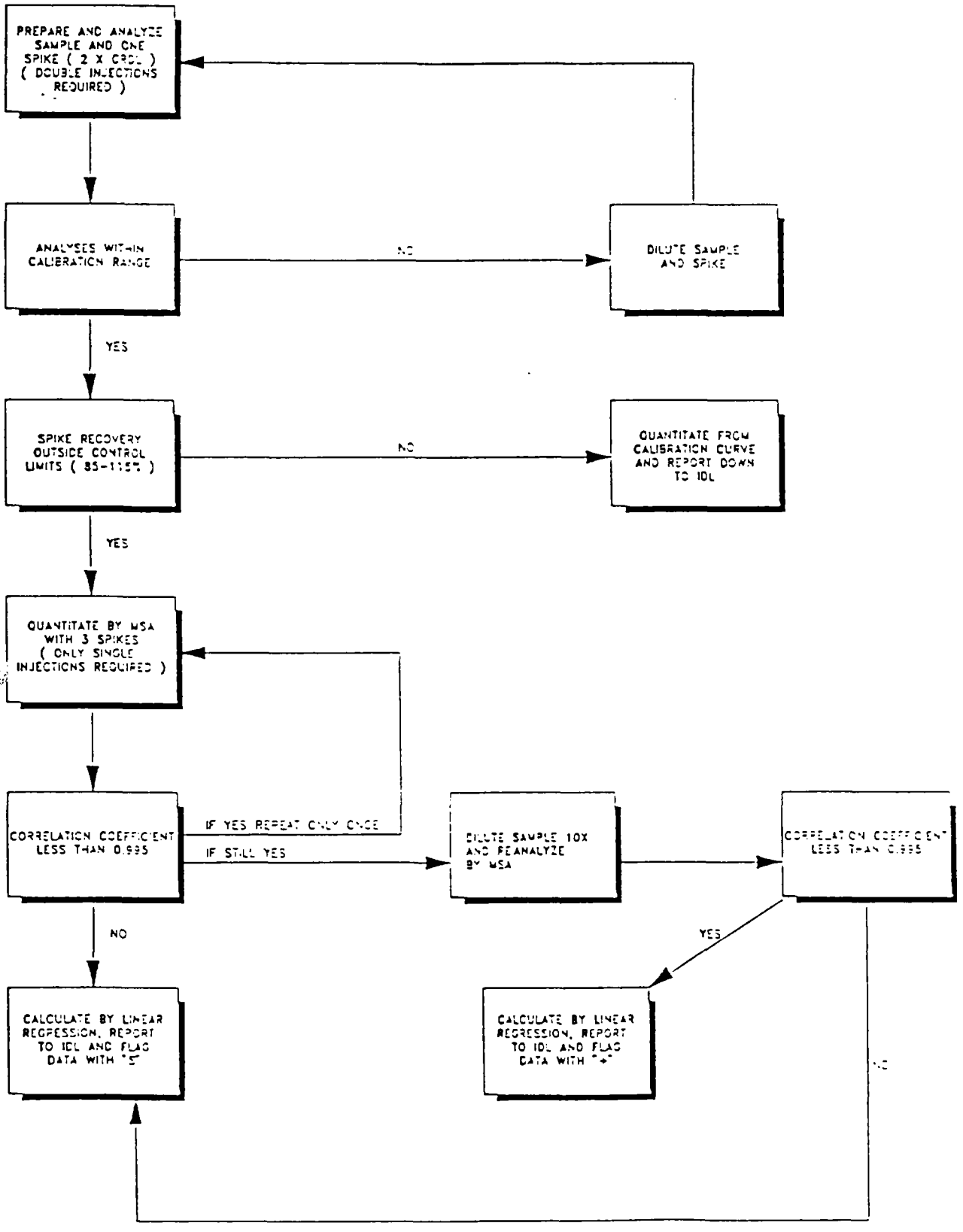
1. Calculate using the instrument concentration mode, or

2. For method of standard additions calculate using linear regression.

[rff-metcont-298]

WARZYN

FURNACE CLP DECISION TREE



Effective Date 4-18-96

ARSENIC - VARIAN 400

Method: AA - Furnace; Direct Injection

Reference: EPA 1984, Method 206.2

"Analytical Methods for Zeeman Graphite Tube Atomizers"-Varian, 1986
Contract Laboratory Program "Statement of Work"

Detection Limit: 0.002 mg/L

Optimum Concentration Range: 0.002 - 0.050 mg/L

Sample Handling: Acidify with nitric acid to pH <2. Analyzed within 6 months. All samples must be digested prior to analysis.

Instrument Conditions:

Instrument Mode:	Absorbance
Calibration Mode:	Concentration
Measurement Mode:	Peak Area
Lamp Current (mA):	20
Slit Width (nm):	1.0
Slit Height:	Normal
Wavelength (nm):	193.7
Sample Introduction:	Sampler Premixed
Time Constant:	0.05
Measurement Time (sec):	1.0
Replicates:	2
Background Correction:	On
Maximum Absorbance:	0.95

FURNACE PARAMETERS

Step	Temp (°C)	Time (sec)	Gas Flow (L/min)	Gas Type	Read Command
1	125	5.0	0.2	NORMAL	NO
2	220	5.0	0.5	NORMAL	NO
3	240	40.0	0.5	NORMAL	NO
4	240	5.0	3.0	NORMAL	NO
5	1200	5.0	3.0	NORMAL	NO
6	1200	10.0	3.0	NORMAL	NO
7	1200	1.0	0.0	NORMAL	NO
8	2600	0.8	0.0	NORMAL	YES
9	2600	2.0	0.0	NORMAL	YES
10	2600	1.0	3.0	NORMAL	NO

Sample Volume: 20 uL

Matrix modifier volume: 5 uL (0.25% nickel nitrate).

Standards to use for curve set-up: 10.0, 20.0, 50.0 ug/L.

Graphite Tube Type: Pyrolitic coated plateau tube

Reagent Preparation:

1. Standard Arsenic Solution (1000 ug/L Arsenic): Pipet 1.00 mL of the 1000 ppm stock arsenic solution into a 1000 mL volumetric flask, add 1/2 mL HNO_3 and dilute to the mark with deionized water. Prepare fresh daily.

2. Calibration standards: (Prepare fresh daily.)

Concentration of Standard	Volume of Arsenic Standard	Dilute to
0 ug/L	0 mL of 1000 ug/L As	100 mL
10 ug/L	1 mL of 1000 ug/L As	100 mL
20 ug/L	2 mL of 1000 ug/L As	100 mL
50 ug/L	5 mL of 1000 ug/L As	100 mL

3. Nickel Nitrate (0.25%): In a 100 mL volumetric flask dissolve 1.25 g of $Ni(NO_3)_2 \cdot 6H_2O$ in D.I. water and dilute to 100 mL. Prepare fresh every 6 months.

Notes:

1. Samples must be diluted to obtain concentrations within the optimum concentration range.

2. Standards are to be prepared in the same acid concentrations as the samples being analyzed.

3. Nickel nitrate is added as a matrix modifier to minimize volatilization losses during the drying and charring steps.

4. The use of background correction is required.

5. High concentrations of phosphorus interfere with this procedure. The gaseous hydride method for arsenic should be used in these cases.

Procedure: For the analysis procedure, refer to the Atomic Absorption Spectrometry, Furnace - Direct Injection section of this manual.

If Arsenic is to be analyzed in concentration mode, calibrate using the 10, 20 and 50 ug/L arsenic standards and the procedures for analyzing in the concentration mode.

[METCONT]

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The absorbances should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, furnace alignment, lamp alignment, graphite tube, etc.).

2. A quality control calibration standard and a blank are to be analyzed, initially and after every 10 samples. If less than 10 samples are analyzed, a calibration standard and blank are still required. The last samples analyzed in the run are to be the calibration standard and blank. These standards must be within the acceptable ranges or the samples run after the last acceptable check standard are to be reanalyzed.

3. Analyze a standard at, or less than, the contract required detection limit of 10 ug/L after the initial calibration verification and blank.

4. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Spike recoveries and duplicate results are to be within acceptable ranges, or data must be flagged appropriately.

5. For every sample analyzed, an analytical spike (at the bench) must be run to verify that standard additions are not required. Criteria for standard additions is:

   a. If the spike recovery is within 85 - 115%, standard additions are not required.

   b. If the spike recovery is outside 85 - 115%, standard additions are required. (See the Furnace Decision Tree for more detail.)

6. An EPA reference sample will be analyzed with each analysis.

Calculations:

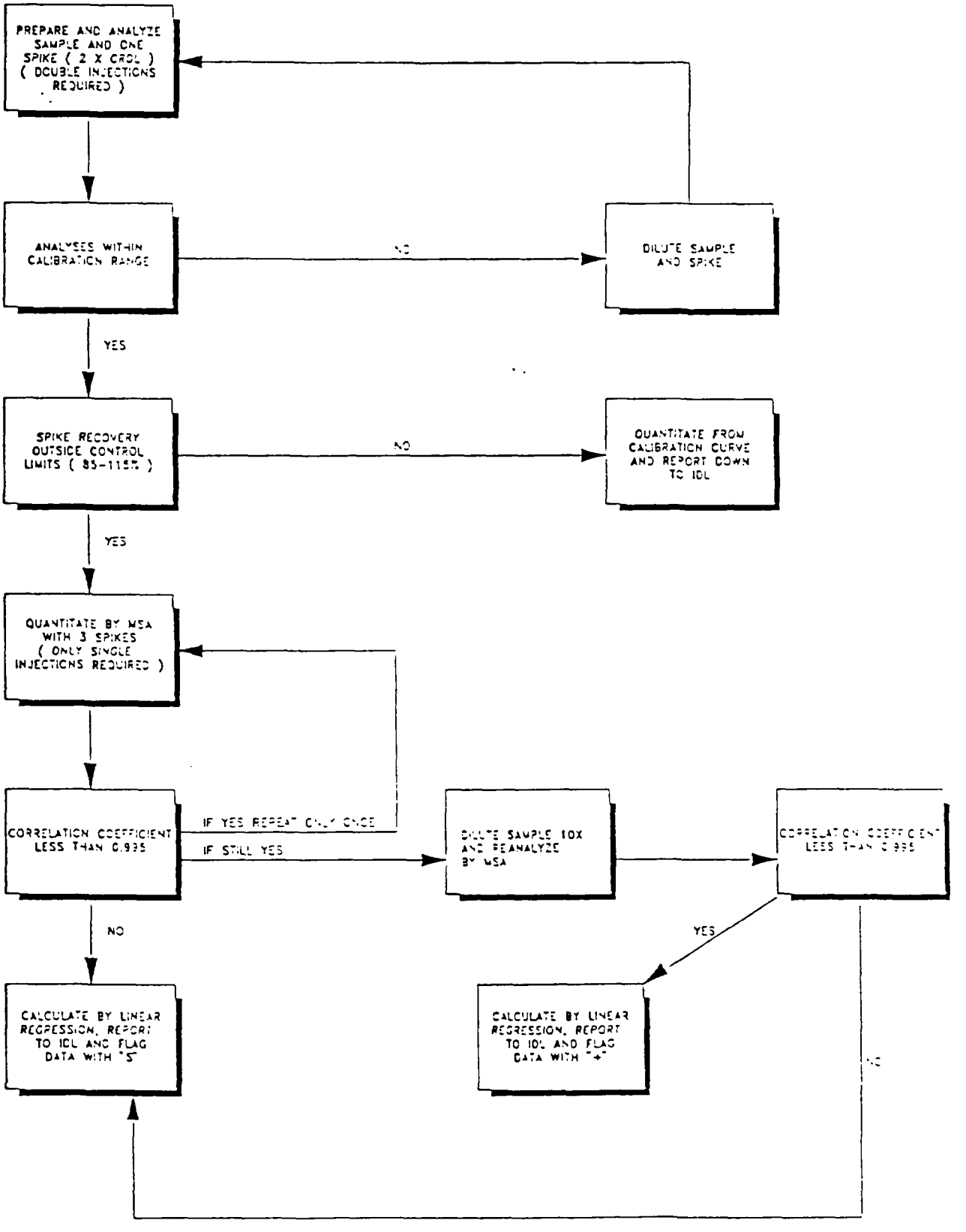
1. Calculate using the instrument concentration mode, or

2. For method of standard additions calculate using linear regression.

[rff-metcont-297]

WARZYN

FURNACE CLP DECISION TREE



Effective Date 4-18-96

CADMIUM - VARIAN 400

Method: AA - Furnace; Direct Injection

Reference: EPA 1984, Method 213.2

"Analytical Methods for Zeeman Graphite Tube Atomizers", Varian, 1986

Contact Laboratory Program, "Statement of Work"

Detection Limit: 0.0002 mg/L

Optimum Concentration Range: 0.0002 - 0.0030 mg/L

Sample Handling: Acidify with nitric acid to pH <2. Drinking waters and filtered groundwater free of particulate matter and organics may be analyzed directly, while wastewaters, leachates, solids, etc. must be digested prior to analysis (refer to appropriate digestion procedures). Analyze within 6 months.

Instrument Conditions:

Instrument Mode:	Absorbance
Calibration Mode:	Concentration
Measurement Mode:	Peak Area
Lamp Current (mA):	3
Slit Width (nm):	0.5
Slit Height:	Normal
Wavelength (nm):	228.8
Sample Introduction:	Sampler Automixing
Time Constant:	0.05
Measurement Time (sec):	1.0
Replicates:	2
Background Correction:	On
Maximum Absorbance:	0.70

FURNACE PARAMETERS

Step	Temp (*C)	Time (sec)	Gas Flow (L/min)	Gas Type	Read Command
1	125	5.0	0.2	NORMAL	NO
2	230	5.0	0.5	NORMAL	NO
3	260	40.0	0.5	NORMAL	NO
4	260	5.0	3.0	NORMAL	NO
5	700	5.0	3.0	NORMAL	NO
6	700	5.0	3.0	NORMAL	NO
7	700	1.0	0.0	NORMAL	NO
8	2000	0.8	0.0	NORMAL	YES
9	2000	2.0	0.0	NORMAL	YES
10	2000	2.0	3.0	NORMAL	NO

[METCONT]

Sample Volume: 12 uL

Matrix Modifier Volume: 4 uL (Monobasic ammonium phosphate)

Standards to use for curve set-up: 1.00, 2.00, 3.00 ug/L

Graphite Tube Type: Pyrolytic coated plateau tube

Reagent Preparation: (Prepare fresh every 6 months unless otherwise noted.)

1. Standard Cadmium Solution (1000 ug/L Cadmium): Pipet 1.00 mL of the 1000 ppm stock cadmium solution into a 1000 mL volumetric flask, add 1/2 mL HNO_3, and dilute to the mark with D.I. water. Prepare fresh daily.

2. Working Cadmium Solution (100 ug/L Cadmium): Pipet 10 mL of the 1000 ug/L cadmium into a 100 mL volumetric flask and dilute to the mark with D.I. water. Prepare fresh daily.

3. Standards (Prepare fresh daily.):

Concentration of Standard	Volume of Cadmium Standard	Dilute to
1.00 ug/L	1 mL of 100 ug/L Cd	100 mL
2.00 ug/L	2 mL of 100 ug/L Cd	100 mL
3.00 ug/L	3 mL of 100 ug/L Cd	100 mL

4. Monobasic Ammonium Phosphate Solution (5000 mg/L): Add 1.0 g of ammonium phosphate (monobasic) to a 100 mL volumetric flask. Dissolve in D.I. water and dilute to volume.

Notes:

1. Samples must be diluted to obtain concentrations within the optimum concentration range.

2. Standards are to be prepared in the same acid concentrations as the samples being analyzed.

3. The use of background correction is required.

4. The cadmium flame or ICP procedure is recommended where concentrations are greater than 0.10 mg/L.

5. Ammonium phosphate is added as a matrix modifier to improve peak shape and allow higher ashing temperatures.

Procedure: For the analysis procedure, refer to the Atomic Absorption Spectrometry, Furnace - Direct Injection section of this manual.

Use of peak area is required.

If cadmium is to be analyzed in concentration mode, use the 1.00, 2.00, and 3.00 ug/L cadmium standards and follow the procedures for analyzing in the concentration mode.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The absorbances should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, furnace alignment, lamp alignment, graphite tube, etc.).

2. A quality control calibration standard and a blank are to be analyzed, initially and after every 10 samples. If less than 10 samples are analyzed, a calibration standard and blank are still required. The last samples analyzed in the run are to be the calibration standard and blank. These standards must be within the acceptable ranges or the samples run after the last acceptable check standard are to be reanalyzed.

3. Analyze a standard at, or less than, the contract required detection limit after the initial calibration verification and blank.

4. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Spike recoveries and duplicate results are to be within acceptable ranges, or data must be flagged appropriately.

5. For every sample analyzed, an analytical spike (at the bench) must be run to verify that standard additions are not required. Criteria for standard additions is:

   a. If the spike recovery is within 85 - 115%, standard additions are not required.

   b. If the spike recovery is outside 85 - 115%, standard additions are required. (See Furnace Decision Tree for more detail.)

6. An EPA reference sample will be analyzed with each analysis.

Calculations:

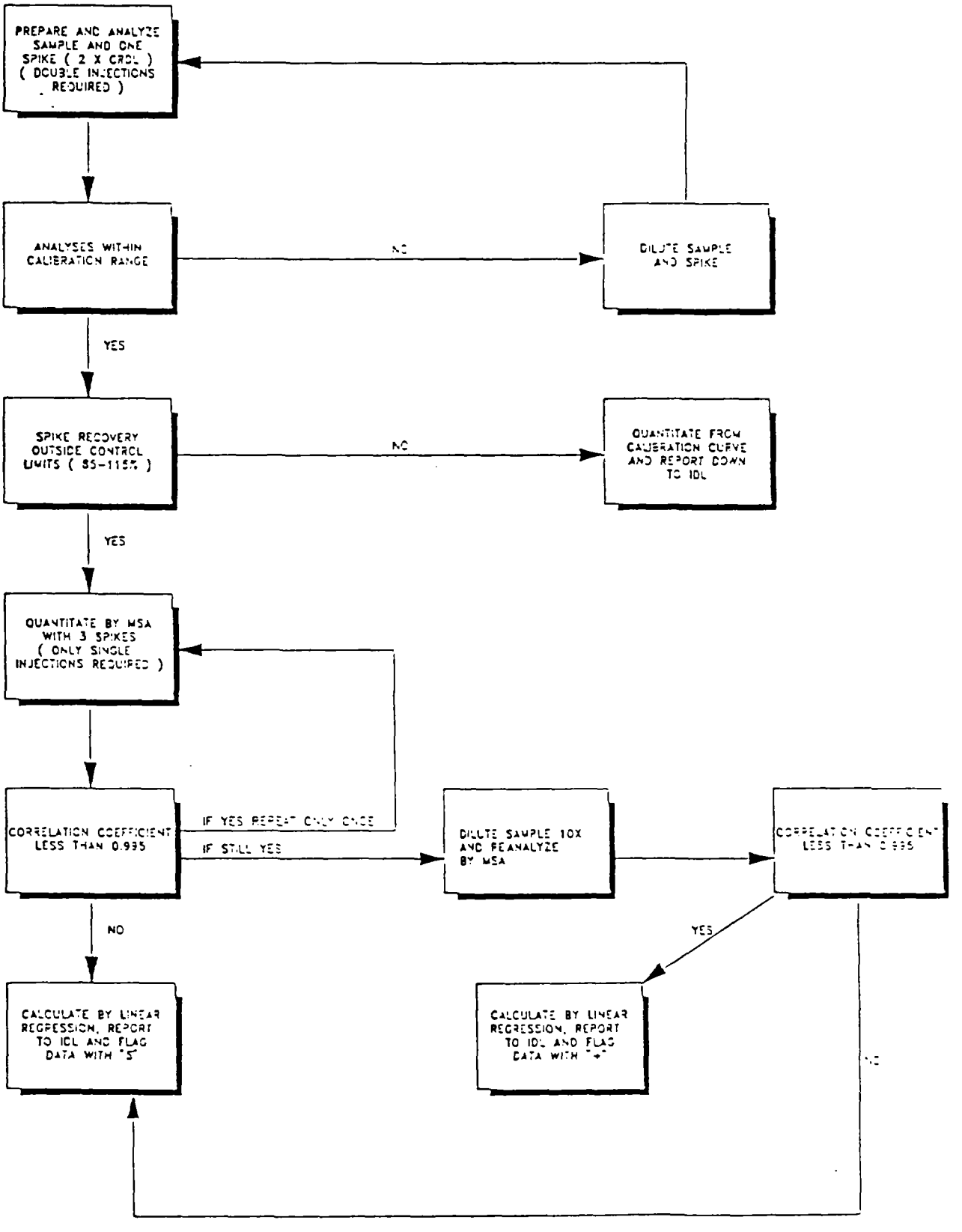
1. Calculate using instrument concentration mode, or

2. For method of standard additions calculate using linear regression.

[rff-metcont-292]

WARZYN

FURNACE CLP DECISION TREE



Effective Date 4-25-90

LEAD - VARIAN 400

Method: AA - Furnace; Direct Injection

Reference:

EPA 1984, Method 239.2

"Analytical Methods for Zeeman Graphite Tube Atomizers", Varian, 1986.

Contract Laboratory Program "Statement of Work"

Detection Limit: 0.003 mg/L

Optimum Concentration Range: 0.003 - 0.050 mg/L

Sample Handling: Acidify with nitric acid to pH < 2. Drinking waters and filtered groundwater free of particulate matter and organics may be analyzed directly, while wastewaters, leachates, solids, etc. must be digested prior to analysis (refer to appropriate digestion procedures). Analyze within 6 months.

Instrument Conditions:

Instrument Mode:	Absorbance
Calibration Mode:	Concentration
Measurement Mode:	Peak Area
Lamp Current (mA):	8
Slit Width	0.5
Slit Height:	Normal
Wavelength	283.3
Sample Introduction:	Sampler Premixed
Time Constant:	0.05
Measurement Time (sec):	1.0
Replicates:	2
Background	On
Maximum Absorbance:	1.40

Furnace Parameters:

Step	Temp (*C)	Time (sec)	Gas Flow (L/Min)	Gas Type	Read Command
1	125	5.0	0.2	NORMAL	NO
2	220	5.0	0.5	NORMAL	NO
3	240	45.0	0.5	NORMAL	NO
4	240	5.0	3.0	NORMAL	NO
5	650	5.0	3.0	NORMAL	NO
6	650	15.0	3.0	NORMAL	NO
7	650	1.0	0.0	NORMAL	NO
8	2200	0.9	0.0	NORMAL	YES
9	2200	2.0	0.0	NORMAL	YES
10	2500	2.0	3.0	NORMAL	NO

Sample Volume: 20 uL

Matrix modifier volume: 5 uL 0.5% w/v Ammonium Phosphate Monobasic or 5 ul of lanthanum nitrate modifier.

Standards to use for curve set-up: 3.0, 20.0, 50.0 ug/L

Graphite Tube Type: Pyrolytic Coated Plateau Tube

Reagent Preparation: (Prepare fresh every 6 months unless otherwise noted.)

1. **Standard lead solution (10.0 mg/L Lead):** Pipet 1.0 mL of the 1000 ppm stock lead solution into a 100 mL volumetric flask, add 1/2 mL HNO_3 and dilute to the mark with deionized water. Prepare fresh daily.

2. **Standard lead solution (100ug/L Lead):** Pipet 1.0 mL of the 10.0 mg/L lead standard into a 100 mL volumetric flash, add 1/2mL HNO_3 and dilute to mark with deionized water. Prepare fresh daily.

3. **Standards:** (Prepare fresh daily.)

Concentration of Standard	Volume of Lead Standard	Dilute to
3.0 ug/L	3 mL of 100 ug/L Pb	100 mL
20.0 ug/L	20 mL of 100 ug/L Pb	100 mL
50.0 ug/L	50 mL of 100 ug/L Pb	100 mL

4. **Ammonium phosphate matrix modifier:** Dissolve 0.5g ammonium phosphate monobasic in 100mL D.I. water.

5. **Lanthanum nitrate matrix modifier:** Dissolve 5.864g of La_2O_3 in 10 ml concentrated nitric acid and dilute to 1 L with D.I. water.

Notes:

1. Samples must be diluted to obtain concentrations within the optimum concentration range.

2. Standards are to be prepared in the same acid concentrations as the samples being analyzed.

3. The use of background correction is required.

4. Ammonium phosphate is added as a matrix modifier to improve peak shape and allow higher ashing temperatures. Ammonium phosphate is the preferred matrix modifier for groundwater, residential wells, and any other samples where chloride or sulfate concentrations are expected to be less than 100 mg/L. Due to its more corrosive nature, lanthanum nitrate should be used as matrix modifier only if chloride and/or sulfate concentrations are expected to exceed 100 mg/L.

Procedure: For the analysis procedure, refer to the Atomic Absorption Spectrometry, Furnace - Direct Injection section of this manual.

If lead is to be analyzed in the concentration mode, calibrate using the 3.0, 20.0 and 50.0 ug/L standards and follow the procedure for analyzing using the concentration mode.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The absorbances should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, furnace alignment, lamp alignment, graphite tube, etc.).

2. A quality control calibration standard of 20.0 ug/L and a blank are to be analyzed, initially and after every 10 samples. If less than 10 samples are analyzed, a calibration standard and blank are still required. The last samples analyzed in the run are to be the calibration standard and blank. These standards must be within the acceptable ranges or the samples run after the last acceptable check standard are to be reanalyzed.

3. Analyze a standard at, or less than, the contract required detection limit after the initial calibration verification and blank.

4. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Spike recoveries and duplicate results are to be within acceptable ranges, or data must be flagged appropriately.

5. For every sample analyzed, an analytical spike (at the bench) must be run to verify that standard additions are not required. Criteria for standard additions is:

   a. If the spike recovery is within 85 - 115%, standard additions are not required.

   b. If the spike recovery is outside 85 - 115%, standard additions are required. (See Furnace Decision Tree for more detail.)

6. An EPA reference sample will be analyzed with each analysis.

Calculations:

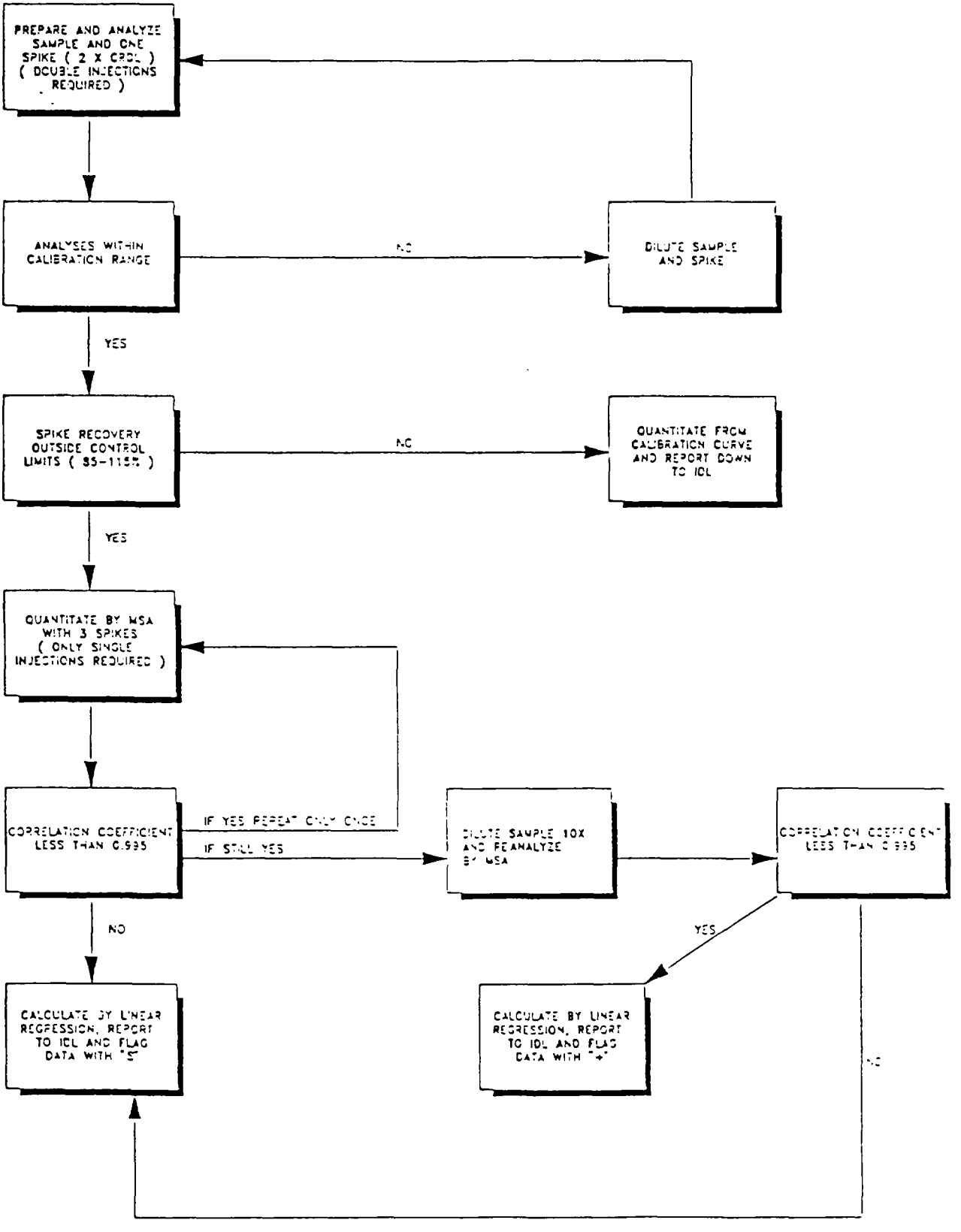
1. Calculate using the instrument concentration mode, or

3. For method of standard additions calculate using linear regression.

[rff-metcont-284]

WARZYN

FURNACE CLP DECISION TREE



Effective Date 4-18-90

SELENIUM - VARIAN 400

Method: AA - Furnace; Direct Injection

Reference: EPA 1984, Method 270.2

"Analytical Methods for Zeeman Graphite Tube Atomizer"-Varian, 1986

Contract Laboratory Program, "Statement of Work"

Detection Limit: 0.002 mg/L

Optimum Concentration Range: 0.002 - 0.050 mg/L

Instrument Conditions:

Instrument Mode:	Absorbance
Calibration Mode:	Concentration
Measurement Mode:	Peak Height
Lamp Current (mA):	18
Slit Width (nm):	1.0
Slit Height:	Normal
Wavelength (nm):	196.0
Sample Introduction:	Sampler Premixed
Time Constant:	0.05
Measurement Time (sec):	1.0
Replicates:	2
Background Correction:	On
Maximum Absorbance:	1.20

FURNACE PARAMETERS

Step	Temp (*C)	Time (sec)	Gas Flow (L/min)	Gas Type	Read Command
1	125	5.0	0.2	NORMAL	NO
2	220	5.0	0.5	NORMAL	NO
3	240	40.0	0.5	NORMAL	NO
4	240	5.0	3.0	NORMAL	NO
5	1400	5.0	3.0	NORMAL	NO
6	1400	10.0	3.0	NORMAL	NO
7	1400	1.0	0.0	NORMAL	NO
8	2600	0.8	0.0	NORMAL	YES
9	2600	2.0	0.0	NORMAL	YES
10	2600	1.0	3.0	NORMAL	NO

[METCONT]

Sample Volume: 20 uL

Matrix Modifier Volume: 5 uL (0.25% nickel nitrate)

Standards to use for curve set-up: 5.0, 10.0, 20.0, 50.0 ug/L.

Graphite Tube Type: Pyrolytic coated plateau tube

Sample Handling: Acidify with nitric acid to pH < 2. Analyze within 6 months.

Reagent Preparation:

1. Standard selenium solution (1000 ug/L Selenium): Pipet 1.00 mL of the 1000 ppm stock selenium solution into a 1000 mL volumetric flask, add 1/2 mL HNO_3 and dilute to the mark with D.I. Prepare fresh daily.

2. Calibration standards: (Prepare fresh daily.)

Concentration of Standard	Volume of Selenium Standard	Dilute to
5.0 ug/L	0.5 mL of 1000 ug/L Se	100 mL
10.0 ug/L	1 mL of 1000 ug/L Se	100 mL
20.0 ug/L	2 mL of 1000 ug/L Se	100 mL
50.0 ug/L	5 mL of 1000 ug/L Se	100 mL

3. Nickel Nitrate (0.25%): In a 100 mL volumetric flask dissolve 1.25 g of $Ni(NO_3)_2 \cdot 6H_2O$ in D.I. water and dilute to 100 mL. Prepare fresh every 6 months.

Notes:

1. Samples must be diluted to obtain concentrations within the optimum concentration range.

2. Chloride (> 800 mg/L) and sulfate (> 200 mg/L) interfere with this selenium procedure. Nickel nitrate is added as a matrix modifier to minimize these interferences.

3. Background correction is required.

Procedure: For the analysis procedure, refer to the Atomic Absorption Spectrometry, Furnace - Direct Injection section of this manual.

For concentration mode, calibrate using the 5.0, 10.0, 20.0 and 50.0 standards and follow the procedure for analyzing using the concentration mode.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The absorbances should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, furnace alignment, lamp alignment, graphite tube, etc.).

2. A quality control calibration standard and a blank are to be analyzed, initially and after every 10 samples. If less than 10 samples are analyzed, a calibration standard and blank are still required. The last samples analyzed in the run are to be the calibration standard and blank. These standards must be within the acceptable ranges or the samples run after the last acceptable check standard are to be reanalyzed.

3. Analyze a standard at, or less than, the contract required detection limit after the initial calibration verification and blank.

4. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Spike recoveries and duplicate results are to be within acceptable ranges, or data must be flagged appropriately.

5. For every sample analyzed, an analytical spike (at the bench) must be run to verify that standard additions are not required. Criteria for standard additions is:

   a. If the spike recovery is within 85 - 115%, standard additions are not required.

   b. If the spike recovery is outside 85 - 115%, standard additions are required. (See Furnace Decision Tree for more detail.)

6. An EPA reference standard will be analyzed with each analysis.

Calculations:

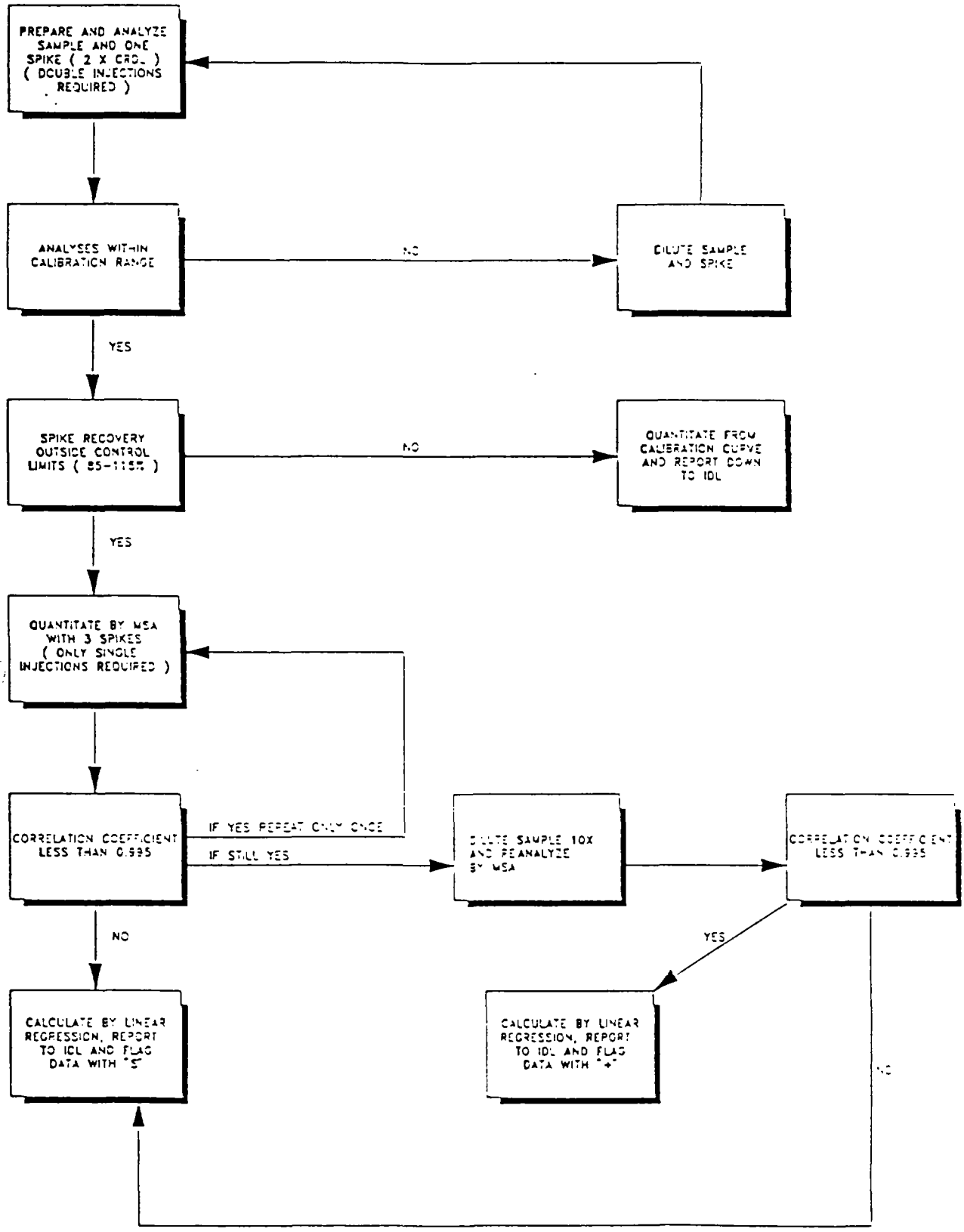
1. Calculate using the instrument concentration mode, or

2. For method of standard additions calculate using linear regression.

[rff-metcont-279]

WARZYN

FURNACE CLP DECISION TREE



Effective Date 4-18-90

SILVER - VARIAN 400

Method: AA - Furnace; Direct Injection

Reference: EPA 1984, Method 272.2

"Analytical Methods for Zeeman Graphite Tube Atomizers", Varian, 1986

Contact Laboratory Program, "Statement of Work"

Detection Limit: 0.001 mg/L

Optimum Concentration Range: 0.001 - 0.010 mg/L

Instrument Conditions:

Instrument Mode	Absorbance
Calibration Mode	Concentration
Measurement Mode	Peak Height
Lamp Position	7
Lamp Current (mA)	4
Slit Width (nm)	0.5
Slit Height	Normal
Wavelength (nm)	328.1
Sample Introduction	Sampler Premixed
Time Constant	0.05
Measurement Time (sec)	1.0
Replicates	2
Background Correction	On
Maximum Absorbance	1.30

FURNACE PARAMETERS

Step	Temp (*C)	Time (sec)	Gas Flow (L/min)	Gas Type	Read Command
1	85	5.0	3.0	NORMAL	NO
2	95	40.0	3.0	NORMAL	NO
3	120	10.0	3.0	NORMAL	NO
4	400	5.0	3.0	NORMAL	NO
5	400	1.0	3.0	NORMAL	NO
6	400	2.0	0.0	NORMAL	NO
7	2000	0.9	0.0	NORMAL	YES
8	2000	2.0	0.0	NORMAL	YES
9	2000	2.0	3.0	NORMAL	NO

Graphite Tube Type: Pyrolytic coated partition tube

Sample Volume: 20 uL

Standards to use for curve set-up: 1.00, 4.00, 10.0 ug/L

Sample Handling: Acidify with nitric acid to pH < 2. Analyze within 6 months.

Reagent Preparation:

1. Standard Silver Solution (1000 ug/L Silver): Pipet 1.00 mL of the 1000 ppm stock silver solution into a 1000 mL volumetric flask, add 1/2 mL HNO_3 and dilute to the mark with D.I. Prepare fresh daily.

2. Working Silver Standard (100 ug/L Silver): Pipet 10 mL of the 1000 ug/L silver standard into a 100 mL volumetric flask and dilute to the mark with D.I. Prepare fresh daily.

3. Standards: (Prepare fresh daily.)

Concentration of Standard	Volume of Silver Standard	Dilute to
1.00 ug/L	1 mL of 100 ug/L Ag	100 mL
4.00 ug/L	4 mL of 100 ug/L Ag	100 mL
10.0 ug/L	10 mL of 100 ug/L Ag	100 mL

Notes:

1. Samples must be diluted to obtain concentrations within the optimum concentration range.

2. Standards are to be prepared in the same acid concentrations as the samples being analyzed.

3. Background correction is required.

4. The use of halide acids should be avoided.

5. Silver standards are light sensitive and tend to plate out on the container walls. Silver standards should be stored in amber glass bottles rather than plastic.

Procedure: For the analysis procedure, refer to the Atomic Absorption Spectrometry, Furnace - Direct Injection section of this manual.

For concentration mode, use the 1.0, 4.0 and 10.0 standards and follow the procedure for analyzing using the concentration mode.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The absorbances should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, furnace alignment, lamp alignment, graphite tube, etc.).

[METCONT]

2. A quality control calibration standard and a blank are to be analyzed, at a minimum, after every 10 samples. If less than 10 samples are analyzed, a calibration standard and blank are still required. The last samples analyzed in the run are to be the calibration standard and blank. These standards must be within acceptable ranges or the samples run after the last acceptable calibration standard are to be reanalyzed.

3. Analyze a standard at, or less than, the contract required detection limit after the initial calibration verification and blank.

4. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Spike recoveries and duplicate results are to be within acceptable ranges, or data must be flagged appropriately.

5. For every sample analyzed, an analytical spike (at the bench) must be run to verify that standard additions are not required. Criteria for standard additions is:

   a. If the spike recovery is within 85 - 115%, standard additions are not required.

   b. If the spike recovery is outside 85 - 115%, standard additions are required. (See Furnace Decision Tree for more detail.)

6. An EPA reference standard will be analyzed with each analysis.

Calculations:

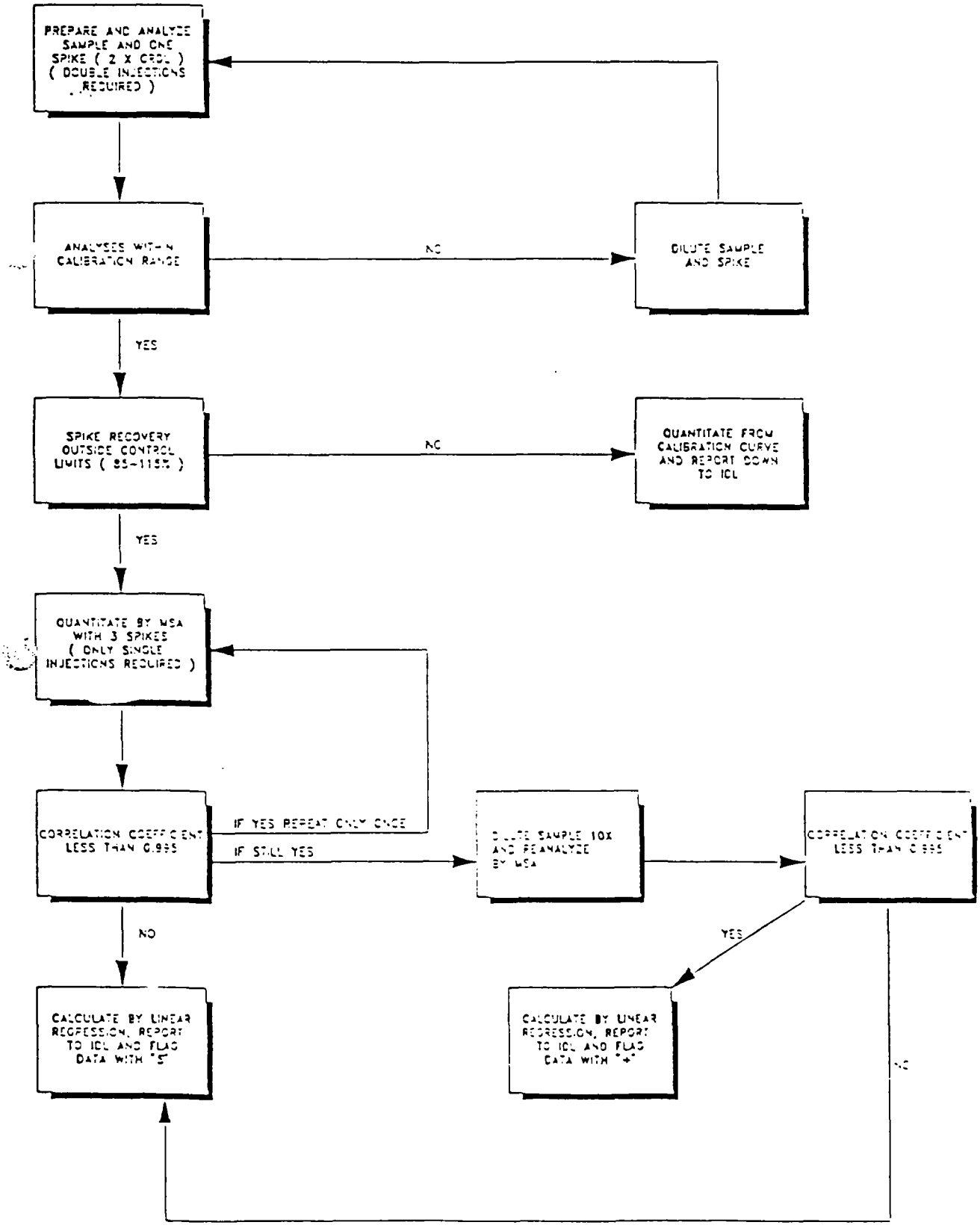
1. Calculate using instrument concentration mode, or

2. For method of standard additions calculate using linear regression.

[rff-metcont-277]

WARZYN

FURNACE CLP DECISION TREE



Effective Date 4-18-90

THALLIUM - 400 VARIAN

Method: AA - Furnace; Direct Injection

Reference: EPA 1984, Method 279.2

"Analytical Methods for Zeeman Graphic Tube Atomizers" - Varian 1986.

Contract Laboratory Program, "Statement of Work".

Detection Limit: 0.005 mg/L

Optimum Concentration Range: 0.005 - 0.050 mg/L

Instrument Conditions:

Instrument Mode:	Absorbance
Calibration Mode:	Concentration
Measurement Mode:	Peak Area
Lamp Current (mA):	10
Slit Width (nm):	0.5
Slit Height:	Normal
Wavelength (nm):	276.8
Sample Introduction:	Sampler Automixing
Time Constant:	0.05
Measurement Time (sec):	1.0
Replicates:	2
Background Correction:	On
Maximum Absorbance:	0.55

FURNACE PARAMETERS

Step	Temp (*C)	Time (sec)	Gas Flow (L/min)	Gas Type	Read Command
1	125	5.0	0.2	NORMAL	NO
2	240	50.0	1.0	NORMAL	NO
3	240	10.0	3.0	NORMAL	NO
4	500	10.0	3.0	NORMAL	NO
5	500	10.0	3.0	NORMAL	NO
6	500	1.0	0.0	NORMAL	NO
7	2400	1.0	0.0	NORMAL	YES
8	2400	2.0	0.0	NORMAL	YES
9	2400	1.0	3.0	NORMAL	NO

Sample Volume: 20 uL

Matrix Modifier Volume: 5 uL (1% H_2SO_4)

Standards to use for curve set-up: 10.0, 20.0, 50.0 ug/L.

Graphite Tube Type: Pyrolytic coated plateau tube

Sample Handling: Acidify with nitric acid to pH <2. Analyze within 6 months.

Reagent Preparation: (Prepare fresh every 6 months unless otherwise noted.)

1. Standard Thallium Solution (1000 ug/L Thallium): Pipet 1.00 mL of the 1000 ppm stock thallium solution into a 1000 mL volumetric flask, add 1/2 mL HNO_3 and dilute to the mark with D.I. water. Prepare fresh every month.

2. Standards (Prepare fresh daily.):

Concentration of Standard	Volume of Thallium Standard	Dilute to
10.0 ug/L	1 mL of 1000 ug/L Tl	100 mL
20.0 ug/L	2 mL of 1000 ug/L Tl	100 mL
50.0 ug/L	5 mL of 1000 ug/L Tl	100 mL

3. H_2SO_4 (1%): Add 5.0 mL of concentrated H_2SO_4 to 400 mL D.I. water. Dilute to 500 mL.

Notes:

1. Samples must be diluted to obtain concentrations within the optimum concentration range.

2. Standards are to be prepared in the same acid concentrations as the samples being analyzed.

3. 1% H_2SO_4 is added as a matrix modifier.

4. The use of background correction is required.

Procedure: For the analysis procedure, refer to the Atomic Absorption Spectrometry, Furnace - Direct Injection section of this manual.

For the use of the concentration mode, use the 10.0, 20.0 and 50.0 standards and follow the procedure for analyzing in the concentration mode.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The absorbances should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, furnace alignment, lamp alignment, graphite tube, etc.).

2. A quality control calibration standard and a blank are to be analyzed, initially and after every 10 samples. If less than 10 samples are analyzed, a calibration standard and blank are still required. The last samples analyzed in the run are to be the calibration standard and blank. These standards must be within the acceptable ranges or the samples run after the last acceptable check standard are to be reanalyzed.

3. Analyze a standard at, or less than, the contract required detection limit after the initial calibration verification and blank.

4. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Spike recoveries and duplicate results are to be within acceptable ranges, or data must be flagged appropriately.

5. For every sample analyzed, an analytical spike (at the bench) must be run to verify that standard additions are not required. Criteria for standard additions is:

   a. If the spike recovery is within 85 - 115%, standard additions are not required.

   b. If the spike recovery is outside 85 - 115%, standard additions are required. (See Furnace Decision Tree for more detail.)

6. An EPA reference standard will be analyzed with each analysis.

Calculations:

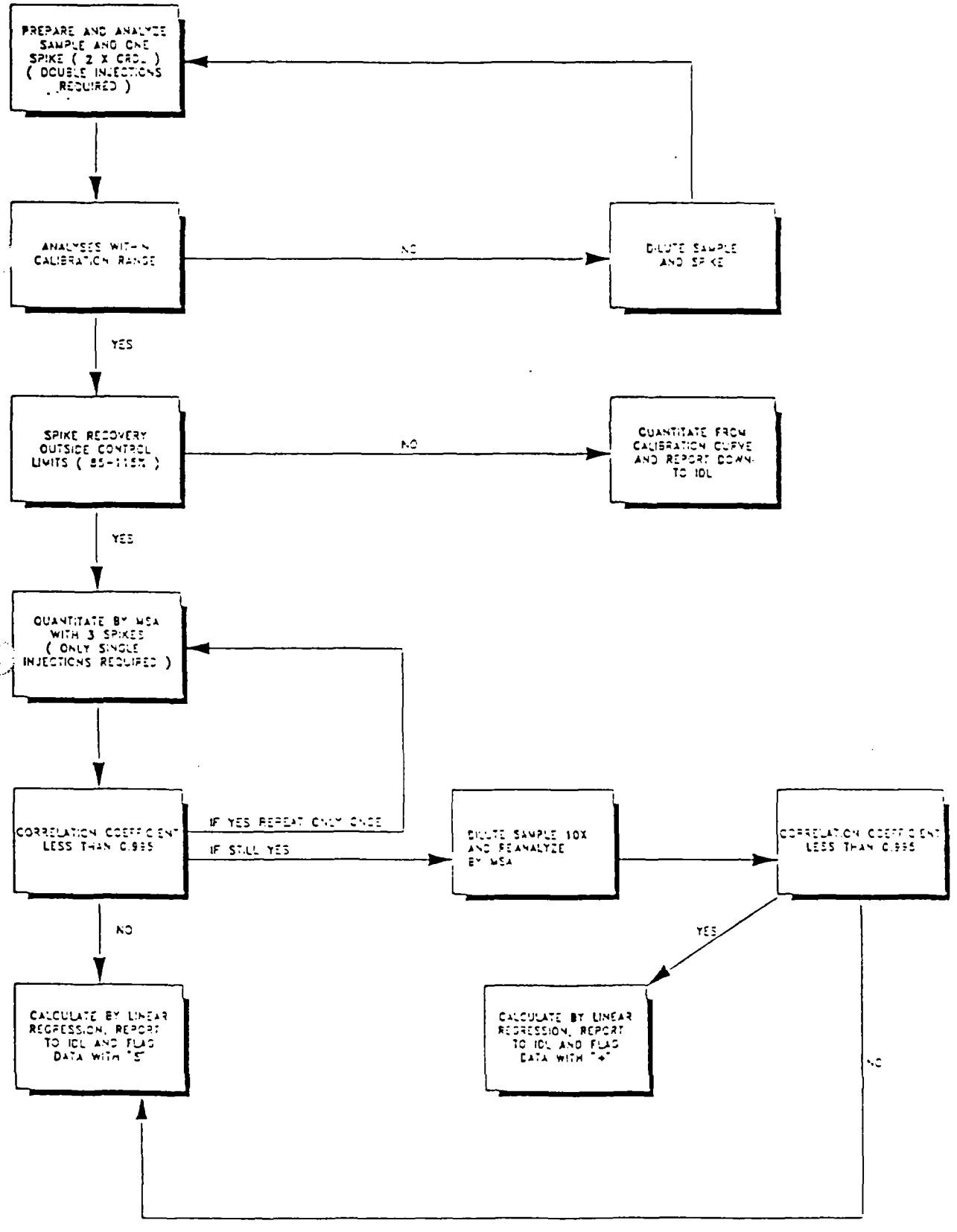
1. Calculate using instrument concentration mode, or

2. For method of standard additions calculate using linear regression.

[rff-metcont-274]

WARZYN

FURNACE CLP DECISION TREE



Effective Date 4-18-90

VANADIUM-VARIAN 400

Method: AA - Furnace; Direct Injection

Reference: EPA 1984, Method 286.2

"Analytical Methods for Zeeman Graphite Tube Atomizers", Varian, 1986

Contact Laboratory Program, "Statement of Work"

Detection Limit: 0.002 mg/L

Optimum Concentration Range: 0.002 - 0.050 mg/L

Instrument Conditions:

Instrument Mode:	Absorbance
Calibration Mode:	Concentration
Measurement Mode:	Peak Area
Lamp Current (mA):	10
Slit Width (nm):	0.2
Slit Height:	Normal
Wavelength (nm):	318.5
Sample Introduction:	Sampler Premixed
Time Constant:	0.05
Measurement Time (sec):	1.0
Replicates:	2
Background Correction:	On
Maximum Absorbance:	1.80

FURNACE PARAMETERS

Step	Temp (*C)	Time (sec)	Gas Flow (L/min)	Gas Type	Read Command
1	95	5.0	3.0	NORMAL	NO
2	130	40.0	3.0	NORMAL	NO
3	1400	10.0	3.0	NORMAL	NO
4	1400	10.0	3.0	NORMAL	NO
5	1400	1.0	0.0	NORMAL	NO
6	2700	0.7	0.0	NORMAL	YES
7	2700	2.0	0.0	NORMAL	YES
8	2700	2.0	3.0	NORMAL	NO

[METCONT]

Sample Volume: 20 uL

Standards to use for curve set-up: 10.0, 20.0, 50.0 ug/L.

Graphite Tube Type: Pyrolytic coated partition tube

Sample Handling: Acidify with nitric acid to pH <2. Analyze within 6 months.

Reagent Preparation: (Prepare fresh every 6 months unless otherwise noted.)

1. Standard vanadium solution (1000 ug/L vanadium): Pipet 1.0 mL of the 1000 ppm stock vanadium solution into a 1000 mL volumetric flask, add 1/2 mL HNO_3 and dilute to the mark with deionized water. Prepare fresh daily.

2. Standards: (Prepare fresh daily.)

Concentration of Standard	Volume of Vanadium Standard	Dilute to
10.0 ug/L	1.0 mL of 1000 ug/L V	100 mL
20.0 ug/L	2.0 mL of 1000 ug/L V	100 mL
50.0 ug/L	5.0 mL of 1000 ug/L V	100 mL

Notes:

1. Samples must be diluted to obtain concentrations within the optimum concentration range.

2. Standards are to be prepared in the same acid concentrations as the samples being analyzed.

3. The use of background correction is required.

4. The use of halide acids should be avoided.

5. Vanadium is a refactory metal, extra care should be taken that sample is not boiled during the digestion (vanadium is easily lost).

Procedure: For the analysis procedure, refer to the Atomic Absorption Spectrometry, Furnace - Direct Aspiration section of this manual.

For the use of concentration mode, use the 10.0, 20.0 and 50.0 standards and follow the procedure for using the concentration mode.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The absorbances should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, flame head alignment, lamp alignment, etc.)

2. A quality control calibration standard of 20.0 ug/L and a blank are to be analyzed, initially and after every 10 samples. If less than 10 samples are analyzed, a calibration standard and blank are still required. The last samples analyzed in the run are to be the calibration standard and blank. These standards must be within the acceptable ranges or the samples run after the last acceptable check standard are to be reanalyzed.

3. Analyze a standard at, or less than, the contract required detection limit after the initial calibration verification and blank.

4. *Duplicate and spike a minimum of 1 out of 10 samples.* If less than 10 samples are analyzed, a duplicate and spike are still required. Spike recoveries and duplicate results are to be within acceptable ranges, or data must be flagged appropriately.

5. For every sample analyzed, an analytical spike (at the bench) must be run to verify that standard additions are not required. Criteria for standard additions is:

   a. If the spike recovery is within 85 - 115%, standard additions are not required.

   b. If the spike recovery is outside 85 - 115%, standard additions are required. (See Furnace Decision Tree for more detail.)

6. An EPA reference sample will be analyzed with each analysis.

Calculations:

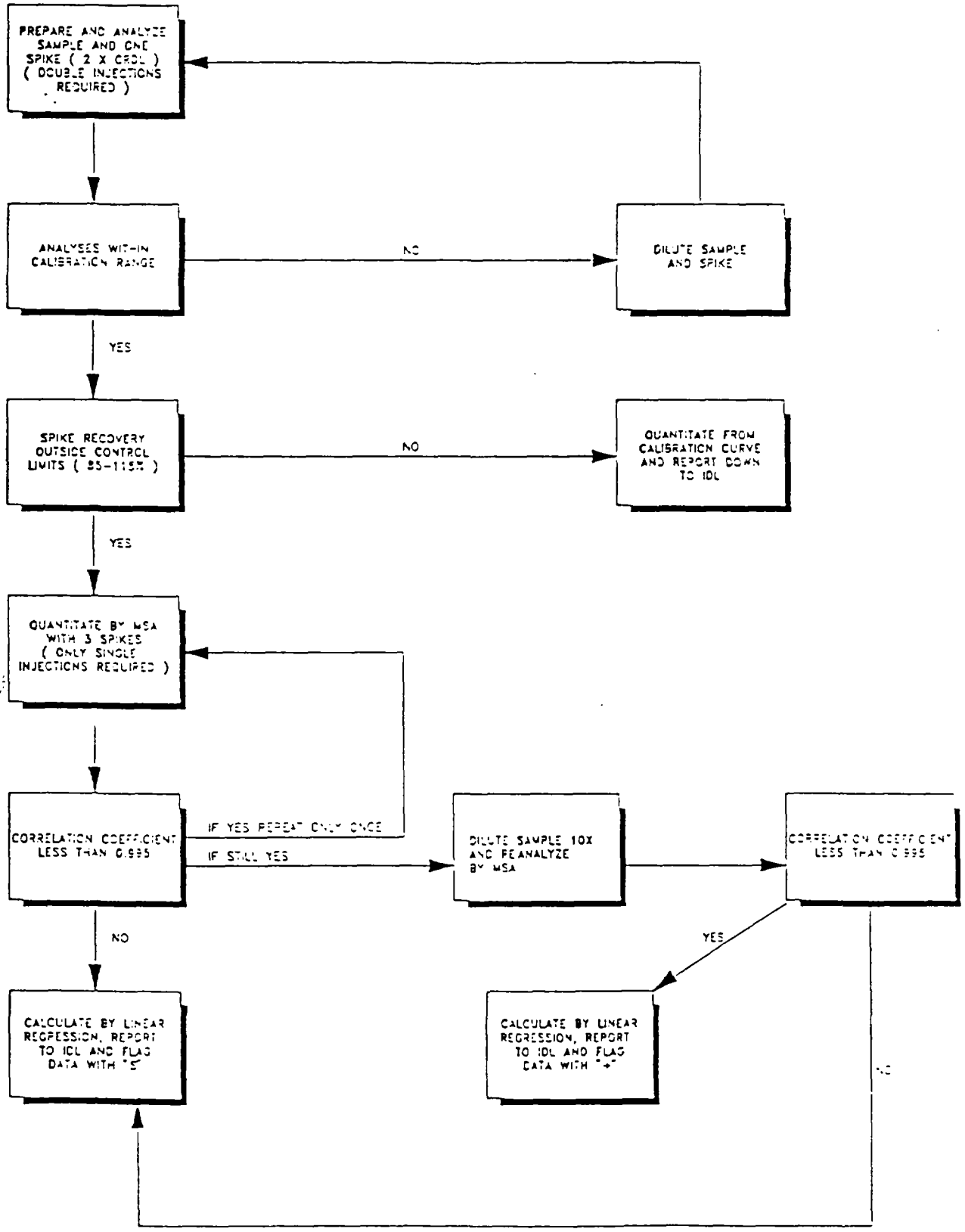
1. Calculate using instrument concentration mode, or

2. For method of standard additions calculate using linear regression.

[rff-metcont-272]

WARZYN

FURNACE CLP DECISION TREE



Effective Date: 3-14-90

ATOMIC ABSORPTION SPECTROMETRY
FLAME - DIRECT ASPIRATION

Scope and Application: Metals in solution can be readily analyzed by Atomic Absorption Spectrometry using either flame or furnace techniques. The flame-direct aspiration can be used for most metals but is generally not as sensitive as the furnace method. Both the air-acetylene and nitrous oxide-acetylene flame techniques are described in this operating procedure as well as the use of emission spectroscopy.

Method: Flame; direct aspiration

Reference: EPA 1984, Section 200

"Analytical Methods for Flame Spectrophotometry", Varian, 1979

Spectr AA - 10/20 Operation Manual, Varian

Sample Handling: Acidify with concentrated nitric acid to pH<2. Drinking waters and filtered groundwater free of particulate matter and organics may be analyzed directly, while wastewaters, leachates, solids, etc. must be digested prior to analysis (refer to appropriate digestion procedures). Samples must be analyzed within 6 months from sampling date.

Reagents and Apparatus:

1. Varian Spectr AA-20
2. Stock and standard metal solutions
3. class A volumetric glassware
4. Instra-analyzed nitric acid
5. Deionized (D.I.) water
6. Hollow cathode element lamps
7. Disposable 10 mL beakers
8. Eppendorf 100-1000 uL pipetter
9. Oxford 5 or 10 ml pipetter
10. Acetylene gas
11. Air supply
12. Nitrous oxide gas
13. Air-acetylene burner head or nitrous oxide-acetylene burner head

Setup:

1. Power on instrument. The computer will automatically start with a memory check. When the first screen appears, it is ready to operate.

   Note: Allow instrument a 1/2 hour warm up period for electronic and optical components to achieve thermal equilibrium before beginning analysis.

2. Power on printer. Check the paper supply.

3. Install the desired element lamp in the lamp turret by depressing the middle white button behind the socket, inserting the lamp, and releasing the button. Ensure that the lamp is secure and that the connections are fitting properly.

   Note: Allow lamp a 10-15 minute warm up period before beginning analysis.

Procedure:

This procedure will outline an analysis as it would be run following the instructions given on sequential computer screens. Note: Any time during setup the "Index" key can be used to go to any screen in the software.

1. Soft key selections allow the operator to develop program, modify program, or automatic run. The typical analysis will be run by selecting "Automatic Run."

   Note: After completing required information on the present screen use the soft keys to call up the next screen.

2. "Sequence Selection". This screen lists the programs on file. Use the "Clear Sequence" soft key to erase the last sequence used, type in the number corresponding to the program desired, and press "Sequence Selection" soft key. This will automatically recall the program.

3. "Sequence Control". The screen is used for autosampler control only. Go to next screen by pressing "Report Format" soft key.

4. Use cursor arrows and numeric keys to enter operator and date. The "Home" key is used to change entries of other parameters.

5. "Sample Labels". Use the cursor arrows and numeric keys to enter labels.

   Note: Sample labels will only be printed if the automatic run is used.

6. "Optimization". This screen is used to optimize wavelength and lamp position.

   a. Ensure lamp is located correctly and is on (lamp is automatically turned on when program is called up).

   b. Select proper slit width.

   c. Release brake ("off") and set approximate wavelength. Set brake ("on") and fine-tune the wavelength to achieve maximum intensity on HCl bar graph. "Rescale" (soft key) as often as necessary to keep graph on scale.

   d. Optimize lamp position by adjusting the adjusting screws on back of the lamp socket. Adjust for maximum intensity on the bar graph. "Rescale" as often as necessary.

   e. If background is used, adjust maximum intensity on background bar graph by 2 set screws on the background corrector housing. Set attenuator ("In" or "Out") if necessary. "Rescale" if necessary.

   f. Record the photomultiplier voltage in the instrument log book. A constantly increasing voltage over time is evidence of decreasing efficiency of the element lamp. Monitor this voltage to determine when element lamps should be replaced.

   Note: HCl and background lamp intensities should match as closely as possible. The attenuator will cut down background intensity. A lower lamp current will lower its intensity.

7. Flame Ignition

   a. Turn on compressed air to 50 psi (35-65 psi)

   b. Turn on acetylene tank, pressure should be 7-15 psi.

   c. Turn on nitrous oxide tank (if necessary - the proper burner head must be in place for ignition to occur). Tank pressure should be 50 psi (35-65 psi).

d. Press "Ignite" key and hold down until flame ignites.

Note: Let burner head warm to equilibrium before analysis; 5 to 10 minutes for an air-acetylene flame, 10 to 15 minutes for a nitrous oxide-acetylene flame.

8. Signal Optimization

a. Press "Signal Optimization" soft key on optimization screen.

b. Adjust burner head using 2 adjusting screws and rotation lever for maximum intensity while aspirating a high standard.

c. Adjust the nebulizer/glass bead by slowly turning the screw directly below the nebulizer.

9. Flame Emission Procedures

a. In this method, no element lamp or background correction is used. Burner head position and wavelength are optimized while aspirating the highest working standard.

b. Turn the burner head full right or left (approximately 30^{o} angle).

c. Select optimization screen.

d. Adjust wavelength for maximum intensity.

e. Press "Emission Setup" soft key.

f. Continue with automatic/non-auto run.

10. Automatic Run (no autosampler)

Note: Only pre-existing programs can be used.

a. Press "Start" key to initialize run. Once a run is started, it can be paused by pressing the "Stop" key, but none of the program parameters can be changed.

b. Press "Instrument Zero" key after program has been recalled to establish a zero instrument baseline.

c. Aspirate standards or sample and press "Read". The instrument will display the std #/sample # on the top of the screen, along with the absorbance.

d. The "Previous Sample"/"Next Sample" soft keys can be used to repeat a specific analysis or move ahead in the sample order, "solution type" can be used to restandardize by starting at "blank".

e. If more than 66 samples and standards are to be run, add them at the end of the run and depress "Previous Sample" key for each sample. Since the sample labels cannot be changed, leave the last few labels blank on the sample labels page, and write them in when the run is completed.

f. Press "Stop" key to pause or end the analysis.

11. Non-automatic Run

Note: A modified or newly developed program can be run in this mode, as well as a pre-existing program.

a. Set up instrument according to previous instruction. Note that the sample labels and report format cannot be printed in this mode.

b. Advance to "Standards" screen by use of soft key on optimization screen or through the "index".

c. Aspirate standards/samples and press "Read" key as in the automatic run.

d. This mode is not limited to the samples. As no labels are printed, these must be written onto the printout by hand.

12. Instrument Shut Down

a. Turn off flame ("Flame Off" key).

b. turn off all gases.

c. Recall program #10 or # (Emission programs), so that no lamp is turned on unnecessarily when the instrument is not turned on.

d. Turn off printer.

e. Turn off instrument.

Effective Date 1-29-90

POTASSIUM - VARIAN 20

Method: Flame Emission: Direct Aspiration

Reference: "Analytical Methods for Flame Spectrophometry, Varian 1979.

Detection Limit: 0.10 mg/L

Optimum Concentration Range: 0.10 - 5.00 mg/L

Sample Handling: Acidify with nitric acid to pH <2. Drinking waters and filtered groundwater free of particulate matter and organics may be analyzed directly, while wastewaters, leachates, solids, etc. must be digested prior to analysis (refer to appropriate digestion procedures). Analyze within 6 months.

Instrument Conditions:

1. Instrument mode: Emission
2. Wavelength: 766.5 nm
3. Slit Width: 1.0
4. Fuel: Acetylene
5. Oxidant: Air
6. Type of flame: Oxidizing, lean, blue
7. Standards to use for curve set-up: 0.50, 1.00, 2.00, 5.00 mg/L.

Reagent Preparation: (Prepare fresh every 6 months unless otherwise noted.)

1. Standard Potassium Solution (100 mg/L Potassium): Pipet 10 mL of the 1000 ppm stock potassium solution into a 100 mL volumetric flask, add 1/2 mL HNO_3, and dilute to the mark with D.I. water.
2. Standards (Prepare fresh daily.):

Concentration of Standard	Volume of Potassium Standard	Dilute to
0.50 mg/L	0.5 mL of 100 mg/L	100 mL
1.00 mg/L	1 mL of 100 mg/L	100 mL
2.00 mg/L	2 mL of 100 mg/L	100 mL
5.00 mg/L	5 mL of 100 mg/L	100 mL

Notes:

1. Samples must be diluted to obtain concentrations within the optimum concentration range.

[VARIAN]

2. Standards are to be prepared in the same acid concentrations as the samples being analyzed.

Procedure: For the analysis procedure, refer to the Atomic Absorption Spectrometry, Flame - Direct Aspiration section of this manual.

If potassium is to be analyzed in concentration mode, use the 1.00 and 5.00 standards and follow the procedure for analyzing in the concentration mode.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The emission readings should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, flame head alignment, etc.).

2. A quality control calibration standard of 1.00 mg/L and a blank are to be analyzed, initially and after every 10 samples. If less than 10 samples are analyzed, a calibration standard and blank are still required. The last samples analyzed in the run are to be the calibration standard and blank. These standards must be within the acceptable ranges or the samples run after the last acceptable check standard are to be reanalyzed.

3. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Spike recoveries and duplicate results are to be within acceptable ranges, or data must be flagged appropriately.

4. An EPA reference sample will be analyzed with each analysis.

Calculations:

1. Plot concentrations vs. absorbance on graph. Determine unknowns using graph, or

2. Calculate using linear regression, or

3. Calculate using the concentration mode.

Effective Date 1-29-90

SODIUM - VARIAN 20

Method: Flame Emission: Direct Aspiration

Reference: "Analytical Methods for Flame Spectrophotometry", Varian, 1979

Contract Laboratory Program, "Statement of Work".

Detection Limit: 1.0 mg/L

Optimum Concentration Range: 1.0 - 100 mg/L

Sample Handling: Acidify with nitric acid to pH <2. Drinking waters and filtered groundwater free of particulate matter and organics may be analyzed directly, while wastewaters, leachates, solids, etc. must be digested prior to analysis (refer to appropriate digestion procedures). Analyze within 6 months.

Instrument Conditions:

1. Set signal to emission. (No lamp is required.)
2. Wavelength: 589.0 nm
3. Slit Width: 0.2 Normal
4. Fuel: Acetylene
5. Oxidant: Air
6. Type of flame: Oxidizing, lean, blue
7. Standards to use for curve set-up: 1.0, 5.0, 10.0, 25.0, 50.0, 75.0, 100.0 mg/L.

Reagent Preparation: (Prepare fresh every 6 months unless otherwise noted.)

1. Standard Sodium Solution (100 mg/L Sodium): Pipet 10 mL of the 1000 ppm stock sodium solution into a 100 mL volumetric flask, add 1/2 mL HNO_3, and dilute to the mark with D.I. water.
2. Standards (Prepare fresh daily.):

Concentration of Standard	Volume of Sodium Standard	Dilute to
1.0 mg/L	1 mL of 100 mg/L Na	100 mL
5.0 mg/L	5 mL of 100 mg/L Na	100 mL
10.0 mg/L	1 mL of 1000 mg/L Na	100 mL
25.0 mg/L	2.5 mL of 1000 mg/L Na	100 mL
50.0 mg/L	5 mL of 1000 mg/L Na	100 mL
75.0 mg/L	7.5 mL of 1000 mg/L Na	100 mL
100.0 mg/L	10 mL of 1000 mg/L Na	100 mL

Notes:

1. Samples must be diluted to obtain concentrations within the optimum concentration range.

2. Standards are to be prepared in the same acid concentrations as the samples being analyzed.

Procedure: For the analysis procedure, refer to the Atomic Absorption Spectrometry, Flame - Direct Aspiration section of this manual but make the following changes:

1. Turn the burner head counter clockwise as far as it will go (approximately a 45° angle).

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The emission readings should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, flame head alignment, etc.).

2. A quality control calibration standard of 25.0 mg/L and a blank are to be analyzed, initially and after every 10 samples. If less than 10 samples are analyzed, a calibration standard and blank are still required. The last samples analyzed in the run are to be the calibration standard and blank. These standards must be within the acceptable ranges or the samples run after the last acceptable check standard are to be reanalyzed.

3. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Spike recoveries and duplicate results are to be within acceptable ranges, or data must be flagged appropriately.

4. An EPA reference sample will be analyzed with each analysis.

Calculations:

1. Plot concentrations vs. absorbance on graph. Determine unknowns using graph.

Effective Date: 3-16-90

MERCURY DIGESTION
Liquid Samples

Scope and Application: This mercury digestion method is applicable to drinking, surface, groundwater, domestic, and industrial wastewaters.

Method: Nitric/sulfuric acid digestion

Reference: EPA 1983, Method 245.1

Sample Handling: Preserve with concentrated HNO_3 to pH <2. Analyze within 28 days of sampling.

Reagents and Apparatus:

1. Water bath set @ 95°C
2. BOD bottles; 300 mL
3. Class A volumetric glassware
4. Instra-analyzed sulfuric acid
5. Instra-analyzed nitric acid
6. Potassium persulfate
7. Potassium permanganate
8. Sodium chloride
9. Hydroxylamine hydrochloride solution
10. Various Class A volumetric pipettes
11. Mercury stock and standard solutions

Reagent Preparation: (Prepare fresh every 6 months, unless otherwise noted.)

1. Sodium chloride-hydrdoxylamine hydrochloride solution: In a 1000ml volumetric flask dissolve 120.0 g of sodium chloride and 120.0 g of hydroxylamine hydrochloride in D.I. water, dilute to 1 liter.

2. Potassium permanganate (5% solution, w/v): In a 1000ml volumetric flask dissolve 50.0 g of potassium permanganate in D.I. water, dilute to 1 liter.

3. Potassium persulfate (5% solution, w/v): In a 1000ml volumetric flask dissolve 50.0 g of potassium persulfate in D.I. water, dilute to 1 liter.

4. Intermediate mercury standard (10.0 mg/L): Transfer 1.0 mL stock mercury (1000 mg/L) solution, plus 0.5 mL nitric acid, into a 100 mL volumetric flask and dilute to the mark with D.I. water. Prepare fresh daily!

5. Working mercury standard (0.100 mg/L): Transfer 1.0 mL of the 10.0 mg/L intermediate standard, plus 0.5 mL nitric acid, into a 100 mL volumetric flask and dilute to the mark with D.I. water. Prepare fresh daily!

Notes:

1. The mercury standards are volatile and unstable. Standards must be prepared daily.

2. Because of the toxic nature of mercury vapor, precaution must be taken to avoid inhalation. Vent the mercury vapor into an exhaust hood or pass the vapor through an absorbing media.

3. Hydroxylamine sulfate may be used rather than hydroxylamine hydrochloride.

4. All blanks, standards, and samples must be carried through the digestion procedure.

5. Interferences:

   a. Potassium permanganate is added to eliminate interferences from sulfide. Concentrations as high as 20 mg/L sulfide as sodium sulfide do not interfere.

   b. Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L have no effect on recovery of mercury from spiked samples.

   c. Seawaters, brines, and industrial effluents, high in chlorides, will require additional potassium permanganate. Care must be taken to ensure that the same amount of potassium permanganate is added to all samples, blanks, and standards so total volume remains constant.

Procedure:

All glassware is to be washed with soap and water, rinsed with tap water, acid rinsed with 10% HNO_3, and final rinsed with D.I. water.

A. Standard Preparation

1. The standard curve is to consist of the following standards:

Standard Concentration
0.00 ug/L
0.50 ug/L
1.00 ug/L
5.00 ug/L
10.0 ug/L

2. Pipet 0, 0.5, 1.0, 5.0, and 10.0 mL aliquots of 0.10 mg/L working stock mercury solution to 300 mL BOD bottles.

3. Add D.I. water to bring volume to 100 mL and continue with the digestion procedure.

B. Sample Preparation:

1. Transfer 100 mL, or an aliquot diluted to 100 mL, to a 300 mL BOD bottle.

   To Spike: Pipette 1.0 mL of 0.10 mg/L mercury standard into the sample bottle.

C. Digestion:

1. Add 5 mL conc. sulfuric acid and 2.5 mL conc. nitric acid to each bottle. Mix by swirling.

2. Add 15 mL potassium permanganate solution to each bottle, mix by swirling. Allow to stand for at least 15 minutes. If the bottle does not remain purple in color, additional potassium permanganate is required. Equal volumes of potassium permanganate must be added to all bottles.

3. Add 8 mL of potassium persulfate solution to each bottle and heat for 2 hours in a water bath maintained at 95°C. Check the bottles periodically throughout the 2 hours to insure the samples remain purple. Add additional potassium permanganate, if needed, to all bottles in the digestion set.

4. Cool to room temperature.

5. Samples are now ready for analysis using the AA-cold vapor procedure.

Quality Control:

1. Refer to the cold vapor SOP for quality control requirements.

Effective Date: 3-16-90

TOTAL MERCURY - AUTOMATED

Scope and Application: This method is applicable to digested drinking, surface, groundwater, domestic, and industrial wastewaters, soils, and sediments. All samples must be digested prior to analysis.

Method: Automated Cold Vapor

Reference: EPA 1983, Method 245.1
SW846, 1982, Method 7471
"Vapor generation Accessory Operation Manual", Varian, 1984
"Statement of Work for Inorganic Analysis, No. 788", EPA 1989

Detection Limits: 0.20 ug/L

Optimum Range: 0.20-10.0 ug/L

Sample Handling: Samples should be capped after digestion.

Reagents and Apparatus:

1. Varian SpectrAA20
2. Varian VGA-76 (cold vapor generator)
3. Varian PSC-56 (autosampler)
4. Sodium chloride
5. Hydroxylamine hydrochloride
6. Stannous chloride
7. Hydrochloric acid
8. Mercury lamp
9. Tygon tubing
10. Whatman #4 filter paper or equivalent

Reagent Preparation: (Prepare fresh every 6 months, unless otherwise noted.)

1. Hydrochloric acid (20% v/v): Add 100 mL of conc. HCl to 200 mL D.I. water in a 500 mL volumetric flask, dilute to 500 mL. PREPARE IN THE HOOD!

2. Stannous chloride (25% w/v): Dissolve 125.0 g stannous chloride in 500 mL of 20% HCL. Prepare fresh every month.

3. Sodium chloride-hydroxylamine hydrochloride solution: Dissolve 120.0 g of sodium chloride and 120.0 g of hydroxylamine hydrochloride in D.I. water, dilute to 1 liter.

Notes:

1. Because of the toxic nature of mercury vapor, precaution must be taken to avoid inhalation. Vent the mercury vapor into an exhaust hood or pass the vapor through an absorbing media.

2. A 10% solution of stannous sulfate may be substituted for stannous chloride.

3. Hydroxylamine sulfate may be used rather than hydroxylamine hydrochloride.

4. Interferences:

   a. Potassium permanganate is added to eliminate interferences from sulfide. Concentrations as high as 20 mg/L sulfide as sodium sulfide do not interfere.

   b. Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L have no effect on recovery of mercury from spiked samples.

   c. Seawaters, brines, and industrial effluents, high in chlorides, will require additional potassium permanganate. during the oxidation step, chlorides are converted to free chlorine which also absorbs at the same wavelength as mercury.

   d. Certain volatile organic materials that absorb at this wavelength may also cause an interference. A preliminary run without reagents can determine if this type of interference is present.

5. Care must be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by leaving digested mercury samples uncapped in the hood for approximately 30 minutes after the additon of the sodium chloride hydroxylamine solution, or allowing a prepared autosampler tray to stand 10-20 minutes before starting an automated analytical run.

6. If particulates remaining in the digested sample cause obstructions in the autosampler tubing, samples can be filtered through Whatman #4 filter paper, or its equivalent, after excess permanganate has been reduced.

Procedure:

For instrument set-up procedures, refer to the Atomic Absorption Spectrometry, Flame section of this manual.

For concentration mode, use 0.5, 1.0, 5.0 and 10.0 ug/L standards to calibrate the instrument.

Instrument Conditions:

Instrument Mode:	Absorbance
Calibration Mode:	Concentration
Measurement Mode:	Integration
Lamp Position:	1
Lamp Current (mA):	4
Slit Width (nm):	0.5
Wavelength (nm):	253.7
Flame:	Air only
Sample Introduction:	Auto Normal
Delay Time:	60
Time Constant:	0.05
Measurement Time (sec):	3.0
Replicates:	3
Background Correction:	On
Air Flow:	0.00
Rinse Rate:	1
Rinse Time:	5.0
Recalibration Rate:	0
Reslope Rate:	0

A. Cold Vapor System Set-up:

1. Insert quartz cell in burner chamber. (Attaches to the air/acetylene burner head.)
2. Visually align cell, checking light path with a white card or paper.
3. Select "Optimization" page and adjust cell for maximum signal.
4. Replace pump tubing on vapor generator.
5. Fill reagent bottles with D.I. water and 25% SnCl (stannous chloride) solution as labelled.

B. Sample Analysis:

1. Prior to analysis, add 6 mL of the sodium chloride-hydroxylamine solution to each bottle to reduce the excess permanganate. Additional sodium chloride-hydroxylamine may be needed to discharge the purple color; equal volumes must be added to all bottles in the digestion set.

2. Pour approximately 12 mL of samples, standards, and blanks into sample tubes and arrange on the autosampler.

3. Turn on argon supply (46 psi recommended).

4. Turn on autosampler power.

5. Turn on vapor generator power (peristaltic pump will run continuously while power is on. Check reagent levels periodically during long runs).

6. Allow pump to operate for 3 to 4 minutes to stabilize flow rates.

7. Start automatic run.

8. Run will stop automatically after it is completed. Press "stop" to release computer.

9. Pull tubing ends out of reagents and let pump empty the lines. Power off pump and release pump tubing. Turn off argon supply.

10. Power off autosampler, printer and AA if done with analyses for the day.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The absorbances should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, tubing, lamp alignment, pump, etc.)

2. A quality control calibration check standard of 5.0 ug/L and a blank are to be analyzed initially and, at a minimum, after every 10 samples. If less than 10 samples are analyzed, a check standard and a blank are still required. The last samples analyzed in the run are to be the check standard and blank. These standards must be within acceptable ranges (80-120%) or the samples run after the last acceptable check standard are to be reanalyzed.

3. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Spike recoveries and duplicate results are to be within acceptable ranges or the data will be flagged appropriately.

4. An EPA or ERA reference standard will be analyzed with each analytical run. The reference standard must be within acceptable limits before any samples are analyzed.

Calculation:

1. Calculate using the concentration mode, or
2. Calculate using linear regression.

Effective:_____

INDUCTIVELY COUPLED PLASMA - ATOMIC EMISSION SPECTROMETRIC METHOD

Scope and Application: Metals in solution can be readily analyzed by atomic emission using an inductively coupled plasma. Dissolved metals are determined in filtered and acidified samples. Total and dissolved metals are determined after appropriate digestion procedures are performed. Appropriate steps must be taken in all analyses to ensure that potential interferences are taken into account. This is especially true when high dissolved solids are present.

Method: Inductively coupled plasma - atomic emission.

Reference: "Inductively Coupled Plasma - Atomic Emission Spectrometric Method of Trace Elements Analysis of Water and Waste", Method 200.7, EPA 1984.

"Inductively Coupled Plasma - Atomic Emission Spectroscopy", Method 6010, SW-846, September, 1986.

"Statement of Work for Inorganic Analysis", SOW No. 788, EPA 1988.

"**Instructions:** Plasma 40 Emission Spectrometer", Perkin-Elmer, 1987.

Sample Handling: Acidify samples with concentrated nitric acid to pH <2. All samples including drinking water and clean groundwaters, must be digested prior to analysis. All samples must be analyzed within 6 months of sampling date.

Reagents and Apparatus:

1. Plasma 40 Perkin-Elmer ICP Spectrometer with Background Correction
2. Argon (liquid: "high purity" or gaseous: "prepurified" grade)
3. Stock and intermediate metal standard solutions
4. EPA and ERA reference standard solutions
5. Nitric acid, conc. (Instra-analyzed or equivalent grade)
6. Hydrochloric acid, conc. (Instra-analyzed or equivalent grade)
7. Class A volumetric glassware
8. Deionized water
9. Disposable 15 mL centrifuge tubes
10. 100 uL Eppendorf pipetter
11. 5 or 10 mL Oxford pipetter
12. Internal Standard - Yttrium or Scandium
13. IBM XT Computer
14. Epson 800 printer

Procedure:

Instrument Set-Up Procedure for Plasma 40:

1. Turn **ON** power switch if necessary. (Routinely left ON throughout week). Allow 2 hours for RF generator to warm up and electronic and optical components to achieve thermal equilibrium.

2. **Perform daily maintenance as specified in Maintenance Procedures:** check pump, pump tubing, and nebulizer tips.

3. Turn argon ON at tank. The first three indicator lights on the ICP (Power, RF ready, Interlock) should be lit.

4. Lock pump tubing in place, raise torch to the "ignite" position, and press "RF on".

5. Ignite plasma and lower torch to the run position (the injector tip should be even with the bottom of the lowest RF coil).

6. Turn on pump and, aspirating rinse water*, allow plasma to stabilize **30 to 40 minutes** before starting analysis.

* Rinse water should be D.I. water with a small amount of liquid detergent (such as Liquinox or Whisk) added to improve wetting of tubing and spray chamber. Approximately 1-2 mL of soap per 500 mL water should be sufficient.

Computer Start-Up Procedure:

1. Turn computer and printer power on. (The computer will automatically start with a memory check).

2. **When the prompt appears type:** Date <Return>. Following the displayed directions enter current date. Next type: Time <Return> and enter current time.

3. **Type:** CD Plasma40 <Return> to enter the Plasma40 directory. Then type: icp <Return> to load software (approximately 10-15 sec).

4. Perform a BEC check as specified in Maintenance Procedures. The BEC value must be within the specified range before any analysis is done.

Sample Analysis:

1. Before starting analysis, for each element to be analyzed:

   a. Select the Spectrum mode of the appropriate element file.

   b. Analyze a single element standard at approximately 2-10X the IDL.

c. Analyze the ICS AB solution.

d. Analyze 1-3 samples representatives of the digestion set.

e. Compare the displayed spectra to check for spectral interferences. Reset background correction points as needed. If there are overlapping peaks or other spectral interferences present, an alternate wavelength or interelement correction must be used. (See table for common spectral interferences.)

2. Select Method mode, and retrieve desired method panel from Library or create a new panel using existing element files. Standard conditions are 25 second read delay, 2 replicates per sample, and report format #2. An internal standard (usually yttrium) must be included in any method. Background correction points are already included in each element file.

3. Add yttrium stock solution (1000 mg/L) as an internal standard to all standards, blanks, and samples in a ratio of 0.1 mL yttrium stock to 10 mL sample. This allows automatic correction for matrix differences in viscosity, surface tension, etc. If the auto sampler is to be used, samples can be pipetted directly into 15 mL centrifuge tubes. Otherwise mix sample and yttrium in small disposable beakers.

4. If auto sampler is to be used, position #1 is the high calibration standard, position #2 is the low calibration standard and position #3 is the calibration blank. Additional calibration standards may be required for some elements.

5. Press F6 to start a manual run or F5 to start an automated run. If running manually, the sample ID number may be typed in before pressing <Return>.

Computer Shut-Down Procedure:

1. When analysis is complete press "ESC". The message "Do you wish to quit method?" should appear.

2. **Type:** Y <Return>. The message "Type ICP to load software" should appear.

3. Turn off computer power switch.

4. Turn off printer.

Caution: Never turn off computer power while still using ICP software. This can cause partial loss of files and other errors.

Instrument Shut-Down Procedure:

1. Aspirate a dilute nitric acid solution (20-50%) for 1 to 2 minutes to clean sample introduction system.

2. Aspirate DI water for 5 minutes to rinse system thoroughly.

Cyanide

AUTOANALYZER

Scope and Application: Ions can be readily analyzed by a flow-injection autoanalyzer. The flow injection design gives the system excellent washout characteristics, to prevent carry over and cross contamination. The autoanalyzer is generally more sensitive and accurate than the manual wet-chemistry techniques.

Method: Flow injection

References: Lachat Instruments, 1986.

Sample Handling: See separate SOP's for requirements.

Reagents and Apparatus:

1. Lachat 3-channel autoanalyzer
2. Stock and standard ion solutions
3. Class A volumetric flasks
4. Class A volumetric pipets
5. Milli-Q water
6. Required interference filters
7. Disposable 4 mL cups
8. Automatic sampler
9. Proportioning pump
10. Injection module
11. Colorimeters
12. Manifolds
13. Columns - if needed
14. Helium gas
15. Computer
16. Printer

Procedure:

A. Instrument Set-Up

1. Depress red power switch on power strip located behind the computer terminal. This will turn on the computer, the screen, and the printer.

2. Depress red power switch on rear power strip on Lachat system.

3. Select manifold and make appropriate hydraulic connections.

   Hydraulic connections:

a. Use correct sample loop length to connect. Lines 1, 4.

b. Line 2 is carrier line.

c. Line 3 goes to manifold.

d. Line 5 goes to waste container.

e. Line 6 comes from sample probe.

f. Connect manifold to flow through cell.

Tension levers should be up when pump tubing is inserted. Snap pump tubing cartridges into place.

4. Insert correct filter.

5. Pump Milli-Q water through lines for 5 minutes by depressing the pump ON button. Check for leaks.

6. Computer - At the C> type in "quikcalc". This calls up the Lachat software and puts you at the master menu. Press <enter>.

7. Put lines into reagents and/or degassed Milli-Q water.

8. Computer - Select "Load/Stop Background Method" on the master menu. Press <enter>.

9. Select appropriate method. Press <enter>.

10. Printer should be set at FONT 0.

11. Pump reagents until a steady baseline is achieved.

12. When using a method with a column (SO_4 or NO_3), the column may be inserted at this point. See method SOP's for more details.

13. For each analytical channel, adjust zero knob so that the baseline is near the bottom of the screen (between .000 - .030).

14. Adjust gain while injecting top standard.

a. Place autosampler probe into the highest standard bottle.

b. After 20-30 seconds, press cycle button on front panel so that LED light is red. This is the load position.

c. After 25 seconds (or less depending on sample loop size), press cycle button so that LED light is green. This is the inject position.

d. Adjust gain knob on detector so that peak reading on the colorimetric is 1.700-1.950.

e. Repeat until gain is properly adjusted.

f. Wipe probe and replace the autosampler probe into the sampler.

15. Select menu item by going into foreground. (Press and hold Alt key, then press Esc key).

    a. Select "Sample Tray Information and Start Analysis" on master menu. Press <enter>.

    b. Press <enter> or type in sample tray reference number if it is a tray which has already been typed in.

    c. Enter tray ID and operator. Check "Display Standards Position in Tray" to insure the tray is set-up properly.

    d. Select "Enter Sample ID's". Press <enter>.

    e. Type in sample information. Check standards will automatically be placed in the tray information portion.

    f. Press Esc once to return to menu.

16. Put tray with samples in appropriate cup locations on autosampler. Position try to the cup containing standard A (usually #35 or so). Select "Start Analysis." Press <enter>.

17. The second screen will ask if the tray has standards or not. If you standardized the first tray of the run and all the check standards are within QC ranges, recalibration for the next tray is <u>not</u> necessary. Select appropriate option. Press <enter>.

18. Press Alt, Esc keys together, to get back to background to view the calibration peaks.

    After calibration is complete:

    - go into the foreground (Press Alt, Esc keys)
    - select "display calibration graph" (Press <enter>)
    - review the data
    - return to the background (Press Alt, Esc keys)

- press "G" for good calibration. Analysis will continue.

- press "R" for re-calibration. Remember to refill standard cups and reposition sample tray before pressing "R"!

B. Instrument Shut-Down

1. Press Alt/Esc keys to get to the foreground. Select "Load/Stop Background Method". Press <enter>. To question-"Stop background (Y/N)?" Press "Yes". Press Esc key to return to main menu.

2. If column is used, stop the pump and disconnect from manifold.

3. Pull lines from reagents into a wash beaker of D.I..

4. Pump D.I. through lines for 2-5 minutes.

5. Pump air through lines until manifold is dry.

6. Turn off pump.

7. Release tubing cartridges and lower tension levers. Release tubing.

8. Turn off main switch on rear power strip.

9. Empty and rinse waste containers, if necessary.

10. Perform back-up on current data files, once a week. (See Section C)

11. Turn off the computer and printer.

C. Backing-up the Data Files

1. Exit to DOS

2. At C> Type: cd\fialab\data Press <enter>

3. At C> Type: copy *.rpt a: Press <enter>
After everything is copied - remove disc.

4. At C> Type: del *.* Press <enter>

5. Are you sure (Y/N)? Type: Y Press <enter>

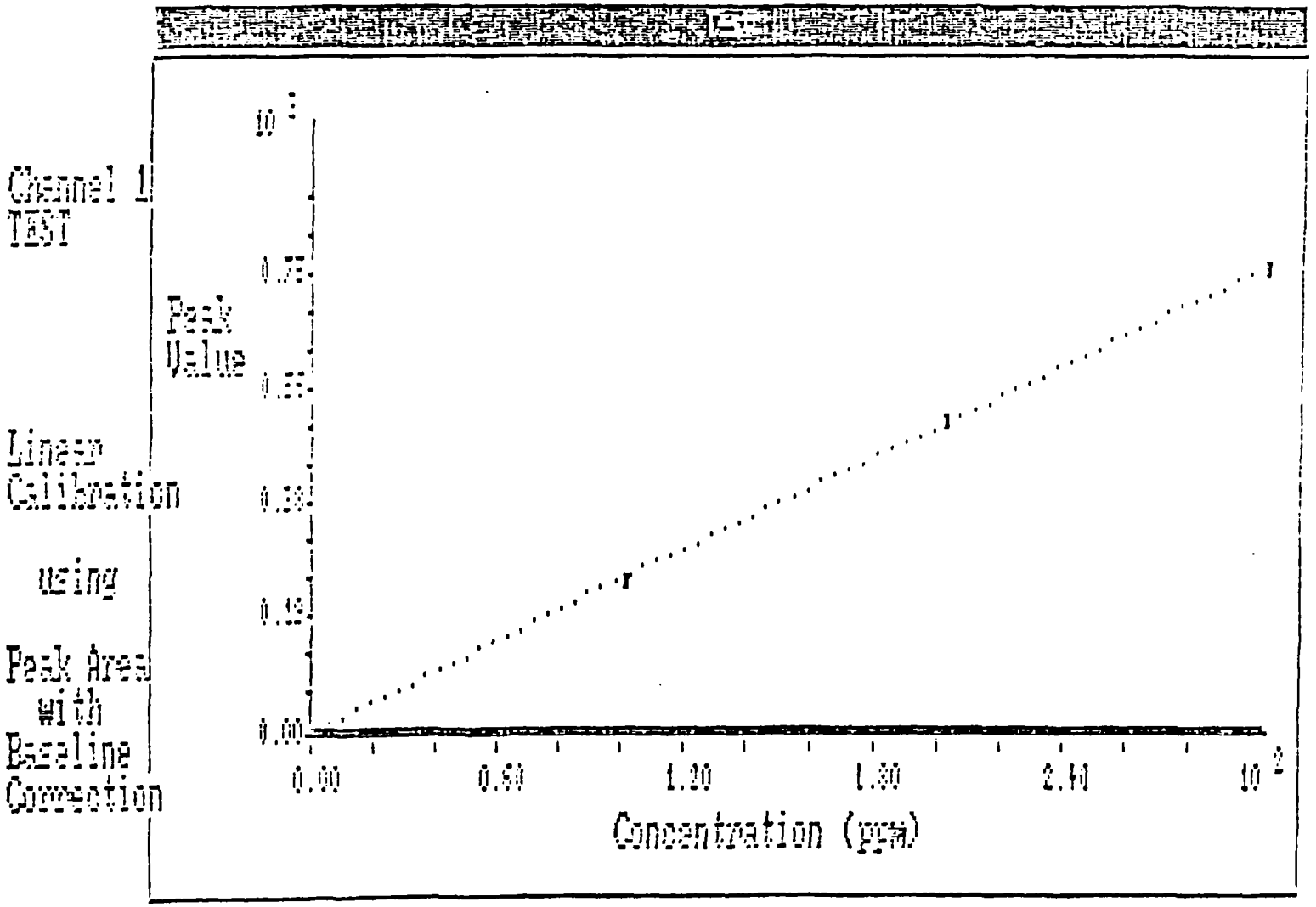
6. At C> Type: cd\ Press <enter>

7. Turn off the red switch on the computer power strip to turn off the computer, printer and screen.

D. Quikchem Calibration

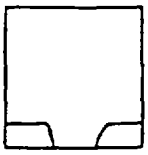
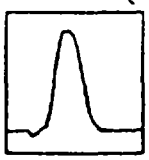
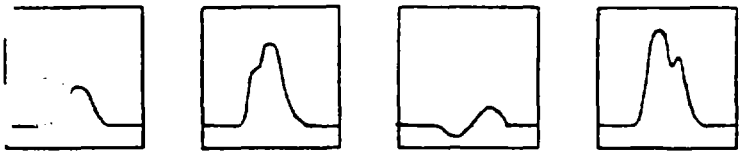
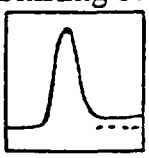
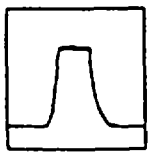
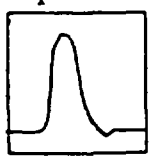
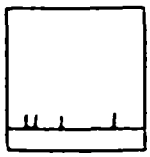
QuikCalc II uses a calibration technique called multisegment linear fitting which gives extensive flexibility to the user. It allows the calibration curve to be defined in terms of individual linear segments which can span each of several standards. Following processing of the calibration standards, a correlation coefficient is calculated for each segment with more than two standards or replicates. It provides important statistical information about each segment and gives the user a high degree of confidence in the determined sample values. See Figure 1.

FIGURE 1



Correlation Coefficient: 0.99985 Press the [Esc] key to continue.

LACHAT TROUBLESHOOTING GUIDE

Problem:	Cause:
Negative peak 	1. Contaminated carrier 2. Bad or no SO_4 column or sample extremely high in hardness 3. Samples high in oxidizing agents
Reproduceable dip when valve switches (before peak) 	1. Bad color reagent 2. Could also be valve turning artifact caused by a highly colored reagent
Odd looking peaks 	1. Index of refraction problem, matrix related (usually acid or pH buffering) 2. Also method interferences: high hardness on SO_4 method, oxidizing samples on nitrate method 3. Bad reagents
Shifting baseline 	1. Flow problem 2. Precipitate build-up on SO_4 manifold tubing
Peak too early/late 	1. Usually flow problem 2. Valve not set to an initial load position state before starting run 3. Incorrect pump setting or other timing problem
Peak cut off in window 	1. Reagents exceeded-reagents improperly prepared 2. Standards incorrectly prepared
Reproduceable dip after peak 	1. Bad column
Small intermittent peaks 	1. Milli-Q or reagents not degassed properly or adequately 2. Waste line coil not installed (for the methods which require it)

Three basic areas of troubleshooting:

1. Fluidics (clogs, old pump tubing, crimp in manifold tubing)
2. Chemistry
3. Timing (not usually a problem after initial development)

BLH/rff
[rff-genpol-604]

Effective Date: 2-12-90

TOTAL CYANIDE - AUTOANALYZER - (HEATED METHOD)

Scope and Application: This method is applicable to distilled groundwater, drinking water, wastewater, sediments and soils. All samples must be distilled prior to analysis with the autoanalyzer. (Refer to SOP # CNDISC.)

Reference: EPA, 1983, Method 335.3
Lachat Instruments, 1986, Method 10-204-00-1-A
Standard Methods, 16th Edition, pages 337-338

Instrument Detection Limit: 0.005 mg/L

Optimum Concentration Range: 0.005 - 0.40 mg/L

Sample Handling: Samples should be capped and refrigerated at 4°C after distillation.

Instrument Conditions:

1. Pump speed: 35
2. Cycle period: 50 seconds
3. Load period: 20 seconds
4. Inject period: 15 seconds
5. Inject to start of peak period: 30 seconds
6. Inject to end of peak period: 78 seconds
7. Gain: 420
8. Zero: 350
9. Interference filter: 570 mm
10. Sample loop: 150 cm (0.80 mm i.d.)
11. Standards for calibration: 0, 0.02, 0.04, 0.10, 0.20, 0.40 mg/L
12. Water Bath 45°C (Position A).

Reagent Preparation: (Prepare fresh every 6 months unless otherwise noted.)

1. Degassed Milli-Q-water - 2 options:

   a. Boil Milli-Q water vigorously for 5 minutes. Cool and store in cubitainer.

   b. Bubble helium, using the fritted gas dispersion tube, through 20 L Milli-Q water for 15-20 minutes. Store in cubitainer.

2. Carrier - 0.25N NaOH:

   In a 1 L volumetric flask, dissolve 10.0 g NaOH in 900 mL DI water. Dilute to the mark and invert several times. Filter through 0.45 micron filter paper. Store in a plastic bottle.

3. Phosphate Buffer - 0.86M (pH 5.2):

   In a 1 L volumetric flask, dissolve 97.0 g KH_2PO_4 in 800 mL degassed MQ water. Add 8.1 mL concentrated (85%) phosphoric acid. Dilute to the mark with degassed MQ water and invert several times.

4. Chloramine-T Solution:

   In a 500 ml volumetric dissolve 2.0 g of chloramine-T in degassed Milli-Q. Dilute to the mark and invert several times. Prepare fresh weekly and store refrigerated.

5. Pyridine - Barbituric Acid Reagent:

   In the fume hood, place 15.0 g barbituric acid in a 1 L beaker and add 100 mL of degassed MQ water, rinsing down the sides of the beaker to wet the barbituric acid. Add 75 mL pyridine (C_5H_5N) while stirring with stir bar. Mix until barbituric acid dissolves. Add 15 mL concentrated HCl and stir. Transfer to a 1 L volumetric flask, dilute to the mark with degassed MQ water and invert several times. Refrigerate. Prepare fresh every 2 months.

6. Stock Cyanide Solution (1000 mg/L):

   Dissolve 0.6275 g KCN and 0.5 g KOH and dilute to 250 mL with D.I. water in a volumetric flask. Prepare fresh every month. Refrigerate. CAUTION: TOXIC!

7. Standard Cyanide Solution (5.0 mg/L):

   Pipet 5 mL of stock cyanide solution into 1 L volumetric flask, add approximately 500 mL DI water. Add 2 mL of 10N NaOH as a preservative and dilute to volume with DI water. Prepare fresh daily. Refrigerate.

8. Cyanide Standards:

Prepare by pipetting the volumes noted below into 250 mL volumetric flasks, adding 50 mL of 1.25N NaOH, and diluting to the mark with degassed MQ water. (The 1.25N NaOH must be added - very important!) Prepare fresh daily.

Concentration of Standard	Letter Identifier	Volume of 5 mg/L working standard (ml)
0.00 mg/L	A	0 mL
0.02 mg/L	B	1.0 mL
0.04 mg/L	C	2.0 mL
0.10 mg/L	D	5.0 mL
0.20 mg/L	E	10 mL
0.40 mg/L	F	20 mL

Note: Computer refers to standards by letter.

NOTES:

1. This chemistry is temperature sensitive. The heated method reduces or eliminates sensitivity drift due to temperature changes.

2. Use wasteline coil to help eliminate air spikes.

3. Any sample dilutions must be diluted with 0.25N NaOH, not water. You may use the carrier or the zero standard for this.

4. Interferences are reduced or eliminated by the distillation procedure. Cyanide analyses suffer from many interferences. See EPA and Standard Methods references for detailed discussion. Information and recommendations for the manual pyridine-barbituric acid color development also apply to this automated method.

5. Samples must be diluted to obtain concentrations within the optimum working range.

6. The gain and zero settings are guidelines and must be optimized each day.

7. Color is an interference, dilute the sample and also manually spike the dilution to confirm the quality of the result.

System Operation:

1. Refer to "Auto Analyzer Operation Start-up Procedure" (IOP # LAA - Section A).

2. Spikes will be distilled at a level of 0.10 mg/L. The calibration check standard is 0.10 mg/L.

3. Analyze a calibration check standard, blank, and known reference standard at the beginning of each run. All standards must be within required control limits before any samples are analyzed.

4. Refer to Auto Analyzer shut-down procedure. (IOP # LAA - Section B).

Quality Control:

1. Establish a standard curve with the standards listed above. The derived concentrations for each calibration standard must read within 10% of the true value. The derived value for the blank must be less than the instrument detection limit.

2. A quality control calibration standard (0.10 mg/L) and blank are to be analyzed initially and at a minimum, after every 10 samples. If less than 10 samples are analyzed, a calibration standard and blank are still required. The last samples analyzed in the run are to be the calibration standard and blank. These standards must be within the acceptable ranges or the samples run after the last acceptable check standard are to be reanalyzed.

3. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Spike recoveries and duplicates are to be within acceptable ranges or data must be flagged appropriately. (These samples must be carried through the distillation step.)

Calculations:

1. Calculate with Lachat QuikChem software, in the concentration mode, using the IBM XT computer. Be sure to calculate any digestion dilution into the final result.

Effective Date 1-29-90

CYANIDE, TOTAL - DISTILLATION

Scope and Application: This method is applicable to the determination of cyanide in drinking water, surface water, groundwater, sludges, soils and industrial wastes.

Methods: *Distillation, Automated Colorimetric*

Reference: EPA 1983, Method 335.2

SW-846, Method 9010

Standard Methods, 16th Edition, Method 412

Detection Limit: 0.005 mg/L

Optimum Range: 0.005 - 0.40 mg/L

Sample Handling: Preserve with sodium hydroxide to pH >12 and refrigerate at 4°C. Analyze samples within 12 days.

Reagents and Apparatus:

1. Cyanide reflux distillation apparatus
2. 25 mL and 50 mL graduated cylinders
3. Vacuum pump
4. Heating mantle
5. 250 mL volumetric flasks
6. Sodium hydroxide
7. Sulfuric acid, concentrated
8. Magnesium chloride
9. Deionized water
10. Bismuth nitrate
11. Sulfamic acid
12. Acetic acid, concentrated
13. Sodium thiosulfate, crystals

Reagent Preparation: (Prepare fresh every 6 months, unless otherwise noted.)

1. Sodium hydroxide (1.25N): Dissolve 50.0 g NaOH in D.I. water and dilute to 1 liter in a volumetric flask. Store in a plastic bottle.

2. Magnesium chloride solution: Dissolve 510.0 g $MgCl_2 \cdot 6H_2O$ in D.I. water and dilute to 1 liter. Store in a plastic bottle.

3. Stock cyanide solution (1000 mg/L): Dissolve 0.6275 g KCN and 0.5 g KOH and dilute to 250 mls with D.I. water in a volumetric flask. Prepare fresh every month. CAUTION: TOXIC! Refrigerate.

4. Standard cyanide solution (5 mg/L): Pipet 5 mL of stock cyanide solution into 1 L volumetric flask containing approximately 500 mL D.I. water and 2 mL of 10N NaOH as a preservative. Dilute to volume with DI water. Prepare fresh weekly. Refrigerate.

5. Bismuth nitrate solution: Dissolve 30.0 g of $Bi(NO_3)_3$ in 100 mL of D.I. water. While stirring, add 250 mL of concentrated acetic acid. Stir until dissolved. Dilute to 1 liter with D.I. water.

6. Sulfamic acid solution: Dissolve 40.0 g of sulfamic acid in D.I. water. Dilute to 1 liter.

Notes:

1. CAUTION: Use care in handling of samples with cyanide because of the toxicity. Avoid skin contact, inhalation, or ingestion. ALWAYS HAVE A RESPIRATOR IN AREA WHEN DOING THIS TEST.

   If a sample begins to bump or back up the tube, quickly increase the flow rate, and turn the heat down (or off) until bumping subsides.

   If a sample does boil over, proceed as follows:

   - Put on respirator
   - Pull inlet tube out
   - Turn heat off (For your proctection, use gloves.)
   - Put sample and heating mantle into hood
   - When sample is cool remove from mantle and heat mantle in hood on high until acid fumes have dissapated.

2. Oxidizing agents, such as chlorine, interfere by decomposing cyanides. If chlorine is believed to present, put a drop of sample on potassium iodide starch paper. If paper turns bluish, add a few crystals of sodium thiosulfate ($Na_2S_2O_3$) to the sample, mix, and retest. Continue adding sodium thiosulfate until free from chlorine. Then, add 0.1 g sodium thiosulfate in excess.

3. Sulfides interfere by forming thiocyanate at a high pH. If sulfides are believed to be present, put a drop of sample on lead acetate test paper treated with acetic acid buffer solution at ph4. Darkening of paper indicates sulfides. If sulfides are present, add 50 mL of bismuth nitrate solution after the air rate is set through the air inlet tube. Mix for 3 minutes prior to addition of H_2SO_4.

   Alternatively, $Cd(NO_3)_2 \cdot 4H_2O$, $CdCO_3$ or $PbCO_3$ can be added after the distillation, but prior to color development. Bismuth nitrate added prior to the distillation process is the preferred choice.

4. Fatty acids, high carbonates, and aldehydes can interfere. Refer to Standard Methods for troubleshooting.

5. High concentrations of NO_3 and NO_2 can give false positive results. If samples contain high concentrations of NO_3 and/or NO_2, add 50 mL of sulfamic acid solution after the air rate is set through the air inlet tube. Mix for 3 minutes prior to addition of H_2SO_4.

Procedure:

1. All glassware is to be soap and water washed, tap rinsed, and deionized rinsed prior to analyses. Dichromate or acetone may also be used to clean the glassware prior to the soap and water wash.

2. Connect and set up cyanide reflux distillation apparatus as shown in Figure 2.

3. Prepare the 0.10 mg/L cyanide digestion standard as follows:

   Add 5 mL of the 5 mg/L cyanide solution to 250 mL of DI water. (Prepare in the distillation flask.)

4. Pour 250 mL of sample into cyanide distilling flask. If a solid or semi-solid sample is to be anaylzed, use a 1.0 g sample size and add 250 mL of D.I. water to the distilling flask. (Record the amount of sample used.) Add an additional 250 mL D.I. water for a total volume of 500 mL in the distillation flask. Add 3-5 boiling chips.

   To Spike: Add 5 mL of the 5 mg/L cyanide solution to the 250 mL of sample, for a final concentration of 0.10 mg/L CN.

5. Using a graduated cylinder, add 50 mL 1.25 N sodium hydroxide to the absorber tube and connect.

6. Turn on vacuum pump and adjust so that one bubble per second enters the distillation flask through the air inlet tube.

7. Slowly add 25 mL concentrated sulfuric acid through the air inlet tube. Rinse the tube with D.I. water and wait for about 2-3 minutes, until the sulfuric acid has been dispersed into the sample.

8. Using a graduated cylinder, add 20 mL magnesium chloride solution into the air inlet tube and rinse the tube with D.I. water.

9. Turn heating mantle on to 60-63% of scale. Watch vacuum rate carefully and adjust as necessary maintaining a rate of one bubble per second. As the temperature increases, bubbling increases, and the solution can be drawn from the absorption tube or blown out the air inlet tube. Reflux for one hour after the sample comes to a boil.

10. Turn off heat and continue vacuum for 15 minutes.

11. Disconnect absorber, DI rinse absorber top into absorbing solution, and shut off vacuum pump.

12. Pour solution from absorber tube into a 250 mL volumetric flask. Using D.I. water, rinse the absorption tube (3 times) and add to the volumetric flask. Dilute to mark with DI water. Mix by inverting.

13. Distillates are ready for analysis. Proceed with Lachat SOP CNAAHC for the automated colorimetric step.

Quality Control:

1. The standard curve does not need to be carried through the distillation procedure.

2. A reagent blank is to be analyzed with each set of samples. This blank is to be carried through the distillation steps as a check for contamination. Date and initial blank container.

3. A quality control calibration standard of 0.10 mg/L cyanide is to be anaylzed with each set of samples. This standard is to be carried through the entire procedure including the distillation step. Date and initial standard container.

4. A known reference standard (LCS) is to be analyzed with each set of samples. This standard is to be carried through the entire procedure including the distillation steps. This standard must be within 80-120 % of the true value and within 95% confidence limits (if available) or the samples are to be reanalyzed.

5. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are anaylzed, a duplicate and spike are still required. Spike recoveries and duplicate results are to be within acceptable ranges.

6. Aqueous and solid/semi-solid samples are separate matrices. Duplicates and spikes are required for each matrix type.

Calculation:

1. Calculate distillate concentration with Lachat QuikChem software, in the concentration mode, using the IBM XT computer. (Be sure to calculate in any distillation dilution into the final result.)

$$\text{ug/L CN} = \frac{(\text{distillate volume,mL})(\text{distillate concentration,mg/L}) \times 1000}{(\text{sample volume,mL})}$$

$$\text{mg/kg CN} = \frac{(\text{distillate volume,mL})(\text{distillate concentration,mg/L})}{(\text{sample weight,gm})}$$

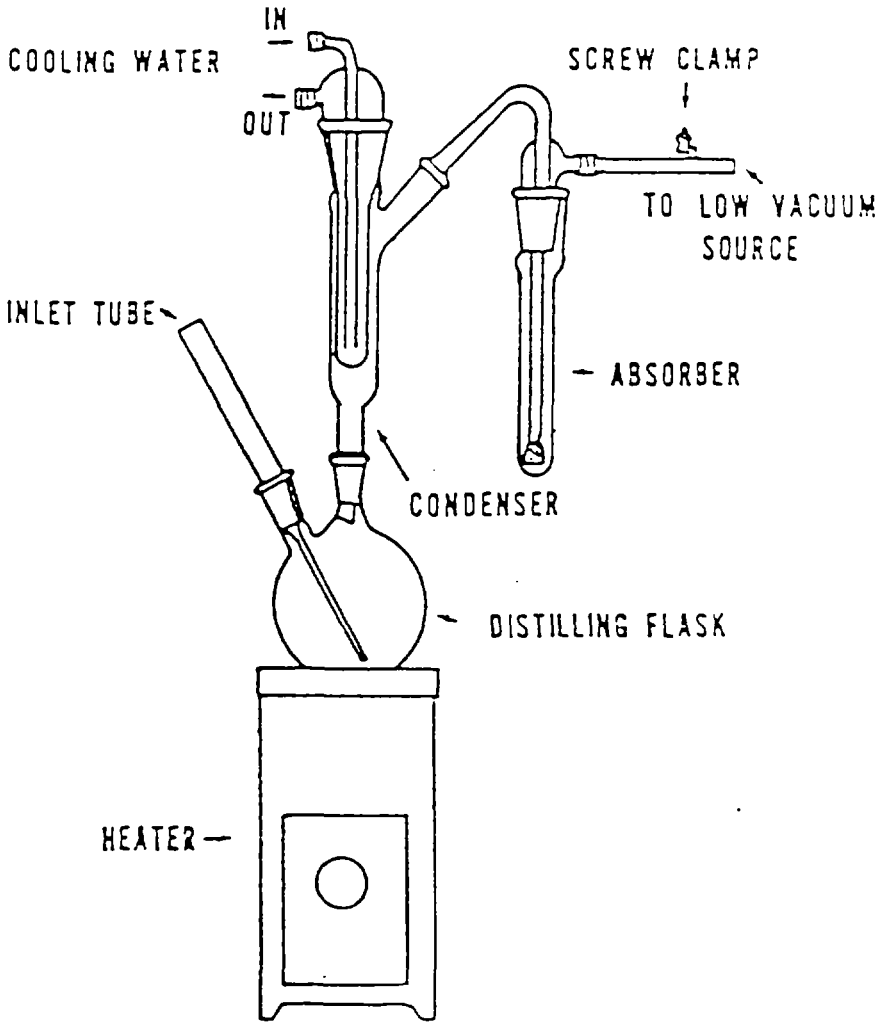


FIGURE 2

CYANIDE DISTILLATION APPARATUS